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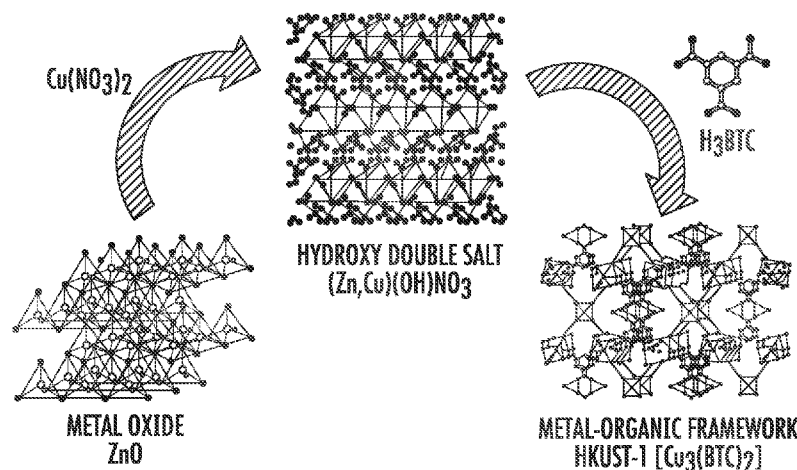
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(54) Title: METAL-ORGANIC FRAMEWORKS AND METHODS OF MAKING AND USE THEREOF



(57) Abstract: Disclosed herein are methods of making metal-organic frameworks. Metal-organic frameworks (MOFs) are a class of crystalline porous materials that exhibit high surface area and large pore volume. The methods can comprise contacting a metal oxide with a metal salt to form a hydroxy double salt, and contacting the hydroxy double salt with an organic linker to form the metal-organic framework. Also disclosed herein is a metal-organic framework comprising copper and 2-aminoterephthalate. The metal-organic frameworks described herein can be used, for example, in a variety of respiration and filter applications, for example for military and/or industrial uses for the removal of toxic gases and/or vapors.



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METAL-ORGANIC FRAMEWORKS AND METHODS OF MAKING AND USE THEREOF

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of priority to U.S. Provisional Application
5 62/352,207, filed June 20, 2016, which is incorporated by reference herein in its entirety.

STATEMENT OF GOVERNMENT SUPPORT

This invention was made with government support under Grant No. W911SR-07-C-0075
and Grant No. W911NF-13-1-0173 awarded by the United States Army Research Office, and
Grant No. W911NF-12-R-0011 awarded by the United States Army. The government has certain
10 rights in the invention.

BACKGROUND

Metal-organic frameworks (MOFs) are a class of crystalline porous materials that exhibit
high surface area and large pore volume. Versatile combinations of metal-organic framework
constituents can enable structural design and pore size control (Eddaoudi M et al. *Science* 2002,
15 295, 469), and post synthetic modification can introduce additional internal functionality
(Sadakiyo M et al. *J. Am. Chem. Soc.* 2014, 136, 13166; Brozek CK and Dincă M. *Chem. Soc.
Rev.* 2014, 43, 5456). While metal-organic frameworks are promising for gas adsorption and
separation, catalysis/photocatalysis, chemical sensing and other applications, the poor synthesis
rates (space-time-yield typically less than 300 kg·m⁻³·d⁻¹) and harsh processing conditions (high
20 temperature and pressure) of traditional solvothermal methods still remain as hurdles for
industrial implementation of metal-organic frameworks and metal-organic framework-
functionalized composites (Stock N and Biswas S. *Chem. Rev.* 2011, 112, 933). Therefore, new
synthetic routes are desired to permit metal-organic framework formation at room temperature.
The methods discussed herein address these and other needs.

25 SUMMARY

In accordance with the purposes of the disclosed compositions and methods, as embodied
and broadly described herein, the disclosed subject matter relates to compositions and methods
of making and using the compositions. More specifically, according to the aspects illustrated
herein, disclosed are metal-organic frameworks and methods of making and use thereof. In some
30 examples, the methods described herein are rapid room-temperature syntheses of metal-organic
frameworks (MOFs), which can be used for industrial implementation and commercialization.

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

The details of one or more embodiments of the invention are set forth in the accompanying drawings and the description below. Other features, objects, and advantages of the invention will be apparent from the description and drawings, and from the claims.

BRIEF DESCRIPTION OF THE FIGURES

The accompanying figures, which are incorporated in and constitute a part of this specification, illustrate several aspects of the disclosure, and together with the description, serve to explain the principles of the disclosure.

Figure 1 is a schematic representation of the rapid room-temperature synthesis route for $\text{Cu}_3(\text{BTC})_2$. ZnO reacts with $\text{Cu}(\text{NO}_3)_2$ to form (Zn, Cu) hydroxy double salt. The (Zn, Cu) hydroxy double salt converts to $\text{Cu}_3(\text{BTC})_2$ via fast anion exchange.

Figure 2 shows the size distribution of ZnO nanoslurries dispersed in deionized water measured by dynamic light scattering (DLS). The average particle size is 252 ± 23 nm, and the polydispersity index is 0.732.

Figure 3 shows the powder X-ray diffraction (XRD) patterns for $\text{Cu}_3(\text{BTC})_2$ synthesized in rapid room-temperature method (top trace) and solvothermal method (middle trace), and simulated $\text{Cu}_3(\text{BTC})_2$ pattern (bottom trace).

Figure 4 shows the percent yield in 1 minute of reaction (circles) and space-time-yield for the rapid room temperature synthesis (diamonds). Insert is an SEM image of a $\text{Cu}_3(\text{BTC})_2$ crystal showing the octahedral shape.

Figure 5 is an SEM image of HKUST-1 crystals obtained from the rapid room-temperature synthesis.

Figure 6 is an SEM image of HKUST-1 crystals obtained from the rapid room-temperature synthesis.

Figure 7 shows the crystal size distribution analyzed from SEM images of HKUST-1 crystals obtained from the rapid room-temperature synthesis (100 measured data points). The average crystal size is 1.17 ± 0.40 μm .

Figure 8 shows an SEM image (upper left panel) of HKUST-1 crystals prepared via rapid synthesis (dispersed on a silicon wafer) and energy dispersive X-ray (EDX) mapping images for C, O and Cu (upper right panel, lower left panel, and lower right panel, respectively) in the HKUST-1 crystals.

Figure 9 shows the EDX spectrum of HKUST-1 crystals prepared via rapid synthesis (dispersed on a silicon wafer) showing that no Zn can be detected by EDX (vertical dashed lines indicate where Zn can be expected).

Figure 10 shows a ToF-SIMS surface mapping (negative ion mode) image for a layer of densely packed HKUST-1 crystals. The results confirm the presence of oxygen.

Figure 11 shows a ToF-SIMS surface mapping (negative ion mode) image for a layer of densely packed HKUST-1 crystals. The results confirm the presence of carbon.

Figure 12 shows a ToF-SIMS surface mapping (negative ion mode) image for a layer of densely packed HKUST-1 crystals. The results confirm the presence of copper.

Figure 13 shows a ToF-SIMS depth profile (positive ion mode) for C^+ , Cu^+ and $^{65}Cu^+$ in a layer of densely packed HKUST-1 crystals.

Figure 14 shows the N_2 adsorption and desorption isotherm for the HKUST-1 powder prepared via rapid synthesis.

Figure 15 shows the X-ray diffraction (XRD) patterns for $Cu_3(BTC)_2$ powder (bottom trace), atomic layer deposition (ALD) ZnO surface after exposure to $Cu(NO_3)_2$ for 1 min (middle trace) and subsequently to H_3BTC for 30 s (top trace). Vertical dotted lines represent the (Zn, Cu) hydroxy double salt.

Figure 16 is an SEM image for HKUST-1 grown on top of (Zn, Cu) hydroxy double salt.

Figure 17 is an SEM image for HKUST-1 grown on top of (Zn, Cu) hydroxy double salt.

Figure 18 shows the FTIR difference spectra for atomic layer deposition (ALD) ZnO in the as-deposited form (bottom trace, Si as background), after exposure to $Cu(NO_3)_2$ for 1 min (second from bottom trace, previous spectrum as background), and after exposure to H_3BTC for 30 s (third from bottom trace, previous spectrum as background) and the final $Cu_3(BTC)_2$ spectrum (top trace, Si as background).

Figure 19 is an HAADF STEM image for the cross section of the $Cu_3(BTC)_2$ grown on atomic layer deposition (ALD) ZnO coated silicon wafer. The outlined box in indicates the location of the STEM and EDX scans shown in Figure 20 and Figure 21.

Figure 20 is an HAADF STEM image of the area indicated in Figure 19 for the cross section of the $\text{Cu}_3(\text{BTC})_2$ grown on atomic layer deposition (ALD) ZnO coated silicon wafer. Scale bars in represents 50 nm.

5 Figure 21 shows the high resolution EDX mapping image of the cross section of the area indicated in Figure 19. Scale bars in represent 50 nm.

Figure 22 shows the Powder X-ray diffraction (XRD) pattern for the Cu-BDC metal-organic framework converted from (Zn, Cu) hydroxy nitrate hydroxy double salt at room temperature (top trace). The simulated Cu-BDC pattern is also shown (bottom trace).

10 Figure 23 shows the powder X-ray diffraction (XRD) pattern for the product obtained by mixing (Zn, Cu) hydroxy double salt with 2-aminoterephthalic acid ($\text{H}_2\text{BDC-NH}_2$). The XRD pattern is similar to Cu-BDC (Figure 22), possibly corresponding to $\text{Cu}(\text{BDC-NH}_2)$.

Figure 24 shows the powder X-ray diffraction (XRD) patterns for the (Zn, Zn) hydroxy double salt (top trace) and IRMOF-3 converted from (Zn, Zn) hydroxy double salt at room temperature (middle trace). The simulated IRMOF-3 pattern is also shown (bottom trace).

15 Figure 25 shows the powder X-ray diffraction (XRD) patterns for the (Zn, Zn) hydroxy acetate hydroxy double salt synthesized with DMF (top trace) and ZIF-8 converted from (Zn, Zn) hydroxy double salt (middle trace). The simulated ZIF-8 pattern is also shown (bottom trace).

20 Figure 26 is a schematic representation of the fabrication procedure for HKUST-1 patterns.

Figure 27 is an SEM image (left panel) and EDX mapping images for a star-shape HKUST-1 pattern.

Figure 28 shows a photo of circular and star-shape HKUST-1 patterns. The outlined box surrounding a section of four stars represents the location of the image shown in Figure 29.

25 Figure 29 shows an optical micrograph image of the section of star patterns made from HKUST-1 indicated by the outlined box in Figure 28.

Figure 30 is an SEM image of a portion of the star patterns made from HKUST-1. The outlined box surrounding a section of the star represents the location of the image shown in Figure 31.

30 Figure 31 is an SEM image of the section of the star pattern made from HKUST-1 indicated by the outlined box in Figure 30.

Figure 32 shows a schematic representation of the rapid room-temperature synthesis route for metal-organic framework coatings onto various form factors.

Figure 33 shows the X-ray diffraction (XRD) patterns for atomic layer deposition (ALD) ZnO coated polypropylene (PP) fiber mat (PP/ZnO, bottom trace) and HKUST-1 grown on PP/ZnO (MOF-PP, top trace).

5 Figure 34 shows the X-ray diffraction (XRD) patterns for atomic layer deposition (ALD) ZnO coated polyacrylonitrile (PAN) nanofiber mat (PAN/ZnO, bottom trace) and HKUST-1 grown on PAN/ZnO (MOF-PAN, top trace).

Figure 35 is an SEM image of HKUST-1 deposited onto polystyrene spheres.

Figure 36 is an SEM image of HKUST-1 deposited onto a silicon wafer.

Figure 37 is an SEM image of HKUST-1 deposited onto polyacrylonitrile nanofibers.

10 Figure 38 is an SEM image of untreated polystyrene microspheres.

Figure 39 is an SEM image of polystyrene microspheres with atomic layer deposition (ALD) ZnO coating.

Figure 40 is an SEM image of HKUST-1 grown on ZnO-coated polystyrene microspheres.

15 Figure 41 is an SEM image of HKUST-1 grown on ZnO-coated polystyrene microspheres.

Figure 42 is an SEM image of ZnO-coated polypropylene (PP) fibers before HKUST-1 rapid synthesis.

20 Figure 43 is an SEM image for ZnO-coated polypropylene (PP) fibers after HKUST-1 rapid synthesis. Insert photo shows the macroscopic uniformity of metal-organic framework growth on the polypropylene fiber mat.

Figure 44 is an SEM image for ZnO-coated polypropylene (PP) fibers after HKUST-1 rapid synthesis.

25 Figure 45 is a cross-sectional TEM image showing uniform HKUST-1 coating on ZnO-coated polypropylene (PP) fibers.

Figure 46 is an SEM image for ZnO-coated polyacrylonitrile (PAN) nanofibers before HKUST-1 rapid synthesis.

30 Figure 47 is an SEM image for ZnO-coated polyacrylonitrile (PAN) nanofibers after HKUST-1 rapid synthesis. Insert optical image shows the uniform metal-organic framework growth on the polyacrylonitrile (PAN) nanofiber mat.

Figure 48 shows the BET surface area for untreated polypropylene (PP) microfibrs and polyacrylonitrile (PAN) nanofibers, and metal-organic framework-coated polypropylene and polyacrylonitrile fibers (MOF-PP, MOF-PAN, respectively).

Figure 49 shows the NH_3 dynamic loading for untreated polypropylene (PP) microfibers and polyacrylonitrile (PAN) nanofibers, and metal-organic framework-coated polypropylene and polyacrylonitrile fibers (MOF-PP, MOF-PAN, respectively).

Figure 50 shows the NH_3 breakthrough curves for untreated polypropylene (PP) and metal-organic framework-coated polypropylene (MOF-PP) fiber mats.

Figure 51 shows the H_2S breakthrough curves for untreated polypropylene (PP) and metal-organic framework-coated polypropylene (MOF-PP) fiber mats.

Figure 52 shows the NH_3 breakthrough curves for untreated polyacrylonitrile (PAN) and metal-organic framework-coated polyacrylonitrile (MOF-PAN) fiber mats.

Figure 53 is a schematic illustration of the crystal structure for the Cu(ATA) metal-organic framework. Color code: Cu (orange), O (red), C (grey), N (blue), H (white).

Figure 54 shows the powder X-ray diffraction (XRD) pattern for the Cu(ATA) metal-organic framework (cross) and comparison with simulated pattern (black). The residue pattern is shown in green.

Figure 55 shows the N_2 isotherm for the Cu(ATA) metal-organic framework.

Figure 56 shows the attenuated total reflectance infrared (ATR-IR) spectrum for the Cu(ATA) metal-organic framework.

Figure 57 is an SEM image of the Cu(ATA) metal-organic framework.

Figure 58 shows the NH_3 breakthrough curve for the Cu(ATA) metal-organic framework.

Figure 59 shows the Cl_2 breakthrough curve for the Cu(ATA) metal-organic framework.

Figure 60 shows a schematic representation of the synthetic procedure for Zr-based metal-organic framework–nanofiber kebab structures on polyamide-6 nanofibers. The metal-organic framework crystal structures are illustrated in the dashed box.

Figure 61a–Figure 61i: Figure 61a is a photo of a free-standing PA-6@TiO₂@UiO-66-NH₂ nanofiber mat. Figure 61b–Figure 61d are SEM images of PA-6@TiO₂@UiO-66-NH₂. Figure 61e–Figure 61i are energy dispersive X-ray mapping images of PA-6@TiO₂@UiO-66-NH₂.

Figure 62a–Figure 62d are SEM images of UiO-66-NH₂ grown on untreated PA-6 nanofibers (Figure 62a–Figure 62b) and ALD TiO₂ coated PA-6 nanofibers (Figure 62c–Figure 62d). Depositing a thin ALD TiO₂ nucleation layer significantly improves the growth uniformity and crystal coverage on the fiber surface.

Figure 63a–Figure 63f: Figure 63a is a SEM image of PA-6@TiO₂@UiO-66. Figure 63b is a TEM image of PA-6@TiO₂@UiO-66. Figure 63c is a SEM image of PA-6@TiO₂@UiO-66-

NH₂. Figure 63d is a TEM image of PA-6@TiO₂@UiO-66-NH₂. Figure 63e is a SEM image of PA-6@TiO₂@UiO-67. Figure 63f is a TEM image of PA-6@TiO₂@UiO-67.

Figure 64a-Figure 64d: SEM images of electrospun PA-6 nanofibers (Figure 64a-Figure 64b) and ALD TiO₂ coated PA-6 nanofibers (Figure 64c-Figure 64d). The average diameter of untreated PA-6 nanofibers measured from SEM images is 37±16 nm.

Figure 65a-Figure 65f: Figure 65a-Figure 65c are XRD patterns of PA-6 nanofibers before and after ALD, MOF-coated nanofibers, and MOF powders. Figure 65d-Figure 65f are N₂ adsorption and desorption isotherms for PA-6@TiO₂ nanofibers with and without MOF coatings and Zr-based MOF powders.

Figure 66a-Figure 66i: SEM image (Figure 66a) and cross-sectional TEM images (Figure 66b-Figure 66d) of UiO-66-NH₂ thin film grown on ALD-TiO₂ coated Si wafer. Figure 66e-Figure 66i are high resolution EDX mapping images of the cross section of UiO-66-NH₂ thin film grown on ALD-TiO₂ coated Si wafer. The rectangle in Figure 66c shows the position of Figure 66d-Figure 66i. The scale bar in Figure 66c represents 30 nm, while the scale bars in Figure 66d-Figure 66i represent 10 nm. The thickness of ALD TiO₂ after solvothermal synthesis of UiO-66-NH₂ thin films measured from Figure 66c-Figure 66d is 15.5±0.2 nm. This thickness is the same with that before the solvothermal synthesis measured via ellipsometry, indicating that the TiO₂ layer was not etched during the synthesis.

Figure 67a-Figure 67e: Figure 67a-Figure 67d are TOF-SIMS surface mapping images of UiO-66-NH₂ thin film grown on ALD-TiO₂ coated Si wafer. Figure 67e is a TOF-SIMS depth profile with 3D reconstruction. C₃H₃⁺ and CN⁻ signals represent the 2-aminoterephthalate linker of UiO-66-NH₂ on the top surface. ZrO⁺ is from the Zr₆O₄(OH)₄¹²⁺ cluster in UiO-66-NH₂, while O⁻ is from both the cluster and the linker. Ti-containing species was not detected on the top surface by TOF-SIMS using either positive or negative ion mode. The TOF-SIMS results are consistent with the cross-sectional TEM images in Figure 66b-Figure 66d.

Figure 68 is a schematic illustration of possible mechanism for the formation of MOF-nanofiber kebab structure during solvothermal synthesis.

Figure 69a-Figure 69e: Figure 69a shows the Catalytic degradation of DMNP using metal-organic framework powder and metal-organic framework-nanofiber kebab structures. Figure 69b shows the UV/Visible absorption spectra for monitoring DMNP hydrolysis. Figure 69c-Figure 69e show the conversion of DMNP to *p*-nitrophenoxide versus reaction time using metal-organic framework powder and metal-organic framework-nanofibers kebabs.

Figure 70 shows the DMNP percent conversion as a function of time during the hydrolysis with untreated PA-6 and ALD TiO₂ coated PA-6 (PA-6@TiO₂) nanofibers. Estimated $t_{1/2}$ values are 3950 min and 1170 min for PA-6 and PA-6@TiO₂, respectively.

Figure 71a-Figure 71f: Kinetic analysis of DMNP degradation with UiO-66 (Figure 71a-Figure 71b), UiO-66-NH₂ (Figure 71c-Figure 71d), and UiO-67 (Figure 71e-Figure 71f). The curves in Figure 71a, Figure 71c, and Figure 71e are plotted using the rate constants derived from the linear fitting in Figure 71b, Figure 71d, and Figure 71f, respectively, based on the assumption of first order reaction kinetics. The reaction kinetics with UiO-66-NH₂ does not fit well to first-order rate equation.

Figure 72a-Figure 72f: Kinetic analysis of DMNP degradation with PA-6@TiO₂@UiO-66 (Figure 72a- Figure 72b), PA-6@TiO₂@UiO-66-NH₂ (Figure 72c- Figure 72d), and PA-6@TiO₂@UiO-67 (Figure 72e- Figure 72f). The curves in Figure 72a, Figure 72c, and Figure 72e are plotted using the rate constants derived from the linear fitting in Figure 72b, Figure 72d, and Figure 72f, respectively, based on the assumption of first order reaction kinetics. The reaction kinetics with PA-6@TiO₂@UiO-66-NH₂ does not fit well to first-order rate equation.

Figure 73 shows the DMNP degradation test with PA-6@TiO₂@UiO-66-NH₂ catalyst removed at $t = 5$ min. The extent of reaction stops immediately after the catalyst is removed, indicating the MOF-nanofiber kebab structures are heterogeneous catalysts. The crude reaction mixture was analyzed using ICP-MS. The concentration of Zr and Ti is as low as 0.10 mg/L and 0.023 mg/L, respectively. The ICP-MS results also confirm that the fast degradation of DMNP is not due to the leaching of Zr⁴⁺ or Ti⁴⁺ into the solution during catalysis.

Figure 74a-Figure 74f: SEM image (Figure 74a) and EDX spectrum (Figure 74b) of PA-6@TiO₂@UiO-66 nanofibers after DMNP degradation experiment. SEM image (Figure 74c) and EDX spectrum (Figure 74d) of PA-6@TiO₂@UiO-66 nanofibers after DMNP degradation experiment. SEM image (Figure 74e) and EDX spectrum (Figure 73f) of PA-6@TiO₂@UiO-67 nanofibers after DMNP degradation experiment. SEM images and EDX results confirm that significant amounts of MOF coatings remain in the MOF-nanofiber composites even after strong agitation during the DMNP hydrolysis tests.

Figure 75a-Figure 75b: XRD (Figure 75a) and N₂ isotherms (Figure 75b) of PA-6@TiO₂@UiO-66-NH₂ before and after the first cycle of DMNP degradation test. The UiO-66-NH₂ coating remains crystalline, and the BET surface area of PA-6@TiO₂@UiO-66-NH₂ decreased from 192 m²/g to 149 m²/g after the first cycle of DMNP degradation test.

Figure 76 shows the cycle test of DMNP degradation using PA-6@TiO₂@UiO-66-NH₂ catalyst. High reactivity was observed in the second cycle with $t_{1/2} = 11.1$ min, and the third cycle still shows noticeable catalytic effect with $t_{1/2} = 96.3$ min.

Figure 77a-Figure 77b: Figure 77a shows the catalytic reaction of GD hydrolysis using metal-organic framework–nanofiber catalysts. Figure 77b shows the conversion of GD versus reaction time during catalysis. Dashed lines are fitted results assuming first order reaction kinetics.

Figure 78 is the ³¹P NMR spectrum of GD during hydrolysis with PA-6@TiO₂@UiO-66 nanofibers.

Figure 79 is the ³¹P NMR spectrum of GD during hydrolysis with PA-6@TiO₂@UiO-66-NH₂ nanofibers.

Figure 80 is the ³¹P NMR spectrum of GD during hydrolysis with PA-6@TiO₂@UiO-67 nanofibers.

DETAILED DESCRIPTION

The metal-organic frameworks and methods described herein may be understood more readily by reference to the following detailed description of specific aspects of the disclosed subject matter and the Examples included therein.

Before the present metal-organic frameworks and methods are disclosed and described, it is to be understood that the aspects described below are not limited to specific synthetic methods or specific reagents, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting.

Also, throughout this specification, various publications are referenced. The disclosures of these publications in their entireties are hereby incorporated by reference into this application in order to more fully describe the state of the art to which the disclosed matter pertains. The references disclosed are also individually and specifically incorporated by reference herein for the material contained in them that is discussed in the sentence in which the reference is relied upon.

In this specification and in the claims that follow, reference will be made to a number of terms, which shall be defined to have the following meanings.

Throughout the description and claims of this specification the word “comprise” and other forms of the word, such as “comprising” and “comprises,” means including but not limited to, and is not intended to exclude, for example, other additives, components, integers, or steps.

As used in the description and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a composition” includes mixtures of two or more such compositions, reference to “an agent” includes mixtures of two or more such agents, reference to “the component” includes
5 mixtures of two or more such components, and the like.

“Optional” or “optionally” means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event or circumstance occurs and instances where it does not.

Ranges can be expressed herein as from “about” one particular value, and/or to “about”
10 another particular value. By “about” is meant within 5% of the value, e.g., within 4, 3, 2, or 1% of the value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are
15 significant both in relation to the other endpoint, and independently of the other endpoint.

It is understood that throughout this specification the identifiers “first” and “second” are used solely to aid in distinguishing the various components and steps of the disclosed subject matter. The identifiers “first” and “second” are not intended to imply any particular order, amount, preference, or importance to the components or steps modified by these terms.

Disclosed herein are methods of making metal-organic frameworks. Metal-organic
20 frameworks (MOFs) are a class of crystalline porous materials that exhibit high surface area and large pore volume. The methods can comprise contacting a metal oxide with a metal salt to form a hydroxy double salt, and contacting the hydroxy double salt with an organic linker to form the metal-organic framework. As used herein, a hydroxy double salt is a layered compound
25 comprising cationic sheets connected by inorganic and/or organic interlamellar anions.

The metal oxide can, for example, comprise a metal selected from the group consisting of Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Pd, Sn, Sr, Ti, V, Zn, and combinations thereof. In some examples, wherein the metal oxide can comprise ZnO, TiO₂, or a combination thereof.

The metal oxide can, for example, comprise a powder, the powder comprising a plurality
30 of particles having an average particle size. “Average particle size,” “mean particle size,” and “median particle size” are used interchangeably herein, and generally refer to the statistical mean particle size of the particles in a population of particles. For example, the average particle size

for a plurality of particles with a substantially spherical shape can comprise the average diameter of the plurality of particles. For a particle with a substantially spherical shape, the diameter of a particle can refer, for example, to the hydrodynamic diameter. As used herein, the hydrodynamic diameter of a particle can refer to the largest linear distance between two points on the surface of the particle. For an anisotropic particle, the average particle size can refer to, for example, the average maximum dimension of the particle (e.g., the length of a rod shaped particle, the diagonal of a cube shape particle, the bisector of a triangular shaped particle, etc.). For an anisotropic particle, the average particle size can refer to, for example, the hydrodynamic size of the particle. Mean particle size can be measured using methods known in the art, such as evaluation by scanning electron microscopy, transmission electron microscopy, and/or dynamic light scattering.

In some examples, the metal oxide can comprise a powder comprising a plurality of particles having an average particle size of 5 nm or more (e.g., 10 nm or more; 20 nm or more; 30 nm or more; 40 nm or more; 50 nm or more; 60 nm or more; 70 nm or more; 80 nm or more; 90 nm or more; 100 nm or more; 125 nm or more; 150 nm or more; 175 nm or more; 200 nm or more; 225 nm or more; 250 nm or more; 275 nm or more; 300 nm or more; 350 nm or more; 400 nm or more; 450 nm or more; 500 nm or more; 600 nm or more; 700 nm or more; 800 nm or more; 900 nm or more; 1,000 nm or more; 1,250 nm or more; 1,500 nm or more; 1,750 nm or more; 2,000 nm or more; 2,250 nm or more; 2,500 nm or more; 3,000 nm or more; 3,500 nm or more; 4,000 nm or more; 4,500 nm or more; 5,000 nm or more; 6,000 nm or more; 7,000 nm or more; 8,000 nm or more; or 9,000 nm or more).

In some examples, the metal oxide can comprise a powder comprising a plurality of particles having an average particle size of 10,000 nm or less (e.g., 9,000 nm or less; 8,000 nm or less; 7,000 nm or less; 6,000 nm or less; 5,000 nm or less; 4,500 nm or less; 4,000 nm or less; 3,500 nm or less; 3,000 nm or less; 2,500 nm or less; 2,250 nm or less; 2,000 nm or less; 1,750 nm or less; 1,500 nm or less; 1,250 nm or less; 1,000 nm or less; 900 nm or less; 800 nm or less; 700 nm or less; 600 nm or less; 500 nm or less; 450 nm or less; 400 nm or less; 350 nm or less; 300 nm or less; 275 nm or less; 250 nm or less; 225 nm or less; 200 nm or less; 175 nm or less; 150 nm or less; 125 nm or less; 100 nm or less; 90 nm or less; 80 nm or less; 70 nm or less; 60 nm or less; 50 nm or less; 40 nm or less; 30 nm or less; 20 nm or less; or 10 nm or less).

The average particle size of the plurality of particles comprising the metal oxide powder can range from any of the minimum values described above to any of the maximum values described above. For example, the metal oxide can comprise a powder comprising a plurality of

particles having an average particle size of from 5 nm to 10,000 nm (e.g., from 5 nm to 5,000 nm; from 5,000 nm to 10,000 nm; from 5 nm to 2,500 nm; from 5 nm to 1,000 nm; from 5 nm to 500 nm; or from 200 nm to 300 nm).

5 In some examples, the plurality of particles of the metal oxide powder can be substantially monodisperse. “Monodisperse” and “homogeneous size distribution,” as used herein, and generally describe a population of particles where all of the particles are the same or nearly the same size. As used herein, a monodisperse distribution refers to particle size distributions in which 70% of the distribution (e.g., 75% of the distribution, 80% of the distribution, 85% of the distribution, 90% of the distribution, or 95% of the distribution) lies
10 within 25% of the median particle size (e.g., within 20% of the median particle size, within 15% of the median particle size, within 10% of the median particle size, or within 5% of the median particle size).

The plurality of particles of the metal oxide powder can comprise particles of any shape (e.g., sphere, rod, cube, rectangle, octahedron, truncated octahedron, plate, cone, prism, ellipse,
15 triangle, etc.). In some examples, the plurality of particles forming the metal oxide powder can have an isotropic shape. In some examples, the plurality particles forming the metal oxide powder can have an anisotropic shape.

In some examples, the methods can further comprise forming a slurry of the metal oxide powder by dispersing the metal oxide powder in a solvent. Dispersing the metal oxide powder in
20 the solvent can be accomplished by mechanical agitation, for example mechanical stirring, shaking, vortexing, sonication (e.g., bath sonication, probe sonication), and the like. Examples of solvents include, but are not limited to, water, alcohols (e.g., methanol, ethanol, n-butanol, isopropanol, n-propanol), carboxylic acids (e.g., acetic acid), chloroform, dimethylformamide (DMF), and combinations thereof.

25 In some examples, the methods can further comprise depositing the metal oxide powder onto a substrate. In some examples, the metal oxide powder can be deposited in a pattern, thereby forming a patterned metal oxide (e.g., to then form a patterned metal-organic framework). Depositing the metal oxide powder can, for example, comprise printing, lithographic deposition, spin coating, drop-casting, zone casting, dip coating, blade coating,
30 spraying, vacuum filtration, slot die coating, curtain coating, or combinations thereof. The substrate can comprise any appropriate substrate, for example, a plurality of polymer particles, a polymer film, a semiconductor wafer, a plurality of polymer fibers, or a combination thereof. In some examples, the substrate can comprise a plurality of polystyrene spheres, a silicon wafer, a

plurality of polypropylene fibers (e.g., a nonwoven polypropylene microfiber mat), a plurality of polyacrylonitrile fibers (e.g., an electrospun polyacrylonitrile nanofiber mat), a plurality of polyamide fibers (e.g., an electrospun polyamide nanofiber mat), or a combination thereof.

In some examples, the metal oxide can comprise a film having a thickness of 1 nm or more (e.g., 2 nm or more, 3 nm or more, 4 nm or more, 5 nm or more, 10 nm or more; 20 nm or more; 30 nm or more; 40 nm or more; 50 nm or more; 60 nm or more; 70 nm or more; 80 nm or more; 90 nm or more; 100 nm or more; 125 nm or more; 150 nm or more; 175 nm or more; 200 nm or more; 225 nm or more; 250 nm or more; 275 nm or more; 300 nm or more; 350 nm or more; 400 nm or more; 450 nm or more; 500 nm or more; 600 nm or more; 700 nm or more; 800 nm or more; 900 nm or more; 1,000 nm or more; 1,250 nm or more; 1,500 nm or more; 1,750 nm or more; 2,000 nm or more; 2,250 nm or more; 2,500 nm or more; 3,000 nm or more; 3,500 nm or more; 4,000 nm or more; 4,500 nm or more; 5,000 nm or more; 6,000 nm or more; 7,000 nm or more; 8,000 nm or more; or 9,000 nm or more).

In some examples, the metal oxide can comprise a film having a thickness of 10,000 nm or less (e.g., 9,000 nm or less; 8,000 nm or less; 7,000 nm or less; 6,000 nm or less; 5,000 nm or less; 4,500 nm or less; 4,000 nm or less; 3,500 nm or less; 3,000 nm or less; 2,500 nm or less; 2,250 nm or less; 2,000 nm or less; 1,750 nm or less; 1,500 nm or less; 1,250 nm or less; 1,000 nm or less; 900 nm or less; 800 nm or less; 700 nm or less; 600 nm or less; 500 nm or less; 450 nm or less; 400 nm or less; 350 nm or less; 300 nm or less; 275 nm or less; 250 nm or less; 225 nm or less; 200 nm or less; 175 nm or less; 150 nm or less; 125 nm or less; 100 nm or less; 90 nm or less; 80 nm or less; 70 nm or less; 60 nm or less; 50 nm or less; 40 nm or less; 30 nm or less; 20 nm or less; or 10 nm or less).

The thickness of the film of metal oxide can range from any of the minimum values described above to any of the maximum values described above. For example, the metal oxide can comprise a film having a thickness of from 1 nm to 10,000 nm (e.g., from 1 nm to 5,000 nm; from 5,000 nm to 10,000 nm; from 1 nm to 2,500 nm; from 1 nm to 1,000 nm; from 1 nm to 500 nm; from 1 nm to 100 nm; from 1 nm to 10 nm; or from 30 nm to 40 nm).

In some examples, the methods can further comprise depositing the film of the metal oxide onto a substrate. In some examples, the metal oxide film can be deposited in a pattern, thereby forming a patterned metal oxide film (e.g., to then form a patterned metal-organic framework). For example, depositing the metal oxide film can comprise printing, lithographic deposition, spin coating, drop-casting, zone casting, dip coating, blade coating, spraying, vacuum filtration, slot die coating, curtain coating, atomic layer deposition, chemical vapor deposition,

electron beam evaporation, thermal evaporation, sputtering deposition, pulsed laser deposition, or combinations thereof. The substrate can comprise any appropriate substrate, for example, a plurality of polymer particles, a polymer film, a semiconductor wafer, a plurality of polymer fibers, or a combination thereof. In some examples, the substrate can comprise a plurality of
5 polystyrene spheres, a silicon wafer, a plurality of polypropylene fibers (e.g., a nonwoven polypropylene microfiber mat), a plurality of polyacrylonitrile fibers (e.g., an electrospun polyacrylonitrile nanofiber mat), a plurality of polyamide fibers (e.g., an electrospun polyamide nanofiber mat), or a combination thereof.

The methods can, in some example, further comprise patterning the metal oxide film
10 before the hydroxy double salt is formed (e.g., to then form a patterned metal-organic framework). In some examples, patterning the metal oxide film can comprise: depositing a radiation sensitive material on the layer of the metal oxide deposited on the substrate; exposing a portion of the radiation sensitive material to radiation; and developing the exposed radiation sensitive material to remove at least a portion of the radiation sensitive material, thereby
15 patterning the radiation sensitive material on the metal oxide film.

The radiation sensitive material can, for example, comprise a photoresist (e.g., a negative photo resist, a positive photoresist), an electron-sensitive resist (e.g., a negative electron-sensitive resist, a positive electron-sensitive resist), or a combination thereof. The radiation can comprise, for example, electromagnetic radiation, electron beam radiation, ion beam irradiation, or a
20 combination thereof.

The portion of radiation sensitive material removed can, for example, comprise the portion of the radiation sensitive material that was exposed to radiation (e.g., the radiation sensitive material can comprise a positive resist). In some examples, the portion of radiation sensitive material removed can comprise the portion of the radiation sensitive material that was
25 not exposed to radiation (e.g., the radiation sensitive material can comprise a negative resist).

In some examples, patterning the metal oxide film can further comprise removing the remainder of the radiation sensitive material after the patterned metal oxide film has been contacted with the metal salt to form a patterned hydroxy double salt, or after the patterned hydroxy double salt has been contacted with the organic linker to form a patterned metal-organic
30 framework.

The metal salt can, for example, comprise a metal selected from the group consisting of Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Pd, Sn, Sr, V, Zn, Zr, and combinations thereof. In some examples, the metal salt can comprise $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{OAc})_2$, ZrCl_4 , or a

combination thereof. In some examples, the metal salt can be provided as a solution, the solution comprising the metal salt and a solvent.

In some examples, the metal oxide can comprise a first metal; and the metal salt can comprise a second metal. In some examples, the first metal and the second metal are different. In some examples, the first metal and the second metal are the same.

The metal oxide and the metal salt can, for example, be provided in a molar ratio of 1:100 or more (e.g., 1:90 or more, 1:80 or more, 1:70 or more, 1:60 or more, 1:50 or more, 1:40 or more, 1:30 or more, 1:20 or more, 1:10 or more, 1:9 or more, 1:8 or more, 1:7 or more, 1:6 or more, 1:5 or more, 2:9 or more, 1:4 or more, 2:7 or more, 3:10 or more, 1:3 or more, 3:8 or more, 2:5 or more, 3:7 or more, 4:9 or more, 1:2 or more, 5:9 or more, 4:7 or more, 3:5 or more, 5:8 or more, 2:3 or more, 7:10 or more, 5:7 or more, 3:4 or more, 7:9 or more, 4:5 or more, 5:6 or more, 6:7 or more, 7:8 or more, 8:9 or more, 9:10 or more, or 19:20 or more).

In some examples, the metal oxide and the metal salt can be provided in a molar ratio of 1:1 or less (e.g., 19:20 or less, 9:10 or less, 8:9 or less, 7:8 or less, 6:7 or less, 5:6 or less, 4:5 or less, 7:9 or less, 3:4 or less, 5:7 or less, 7:10 or less, 2:3 or less, 5:8 or less, 3:5 or less, 4:7 or less, 5:9 or less, 1:2 or less, 4:9 or less, 3:7 or less, 2:5 or less, 3:8 or less, 1:3 or less, 3:10 or less, 2:7 or less, 1:4 or less, 2:9 or less, 1:5 or less, 1:6 or less, 1:7 or less, 1:8 or less, 1:9 or less, 1:10 or less, 1:20 or less, 1:30 or less, 1:40 or less, 1:50 or less, 1:60 or less, 1:70 or less, 1:80 or less, or 1:90 or less).

The metal oxide and the metal salt can be provided in a molar ratio that ranges from any of the minimum values described above to any of the maximum values described above. For example, the metal oxide and the metal salt can be provided in a molar ratio of from 1:100 to 1:1 (e.g., from 1:100 to 1:50, from 1:50 to 1:1, from 1:20 to 1:1, from 1:10 to 1:1, or from 1:5 to 4:5).

The organic linker can, for example, comprises trimesic acid, 2-methylimidazole, biphenyldicarboxylic acid, terephthalic acid, derivatives thereof, or a combination thereof. Examples of derivatives of terephthalic acid that can be used as the organic linker include, but are not limited to, 2-aminoterephthalic acid, 2-chloroterephthalic acid, 2-nitroterephthalic acid, 2,5-diaminoterephthalic acid, and the like.

In some examples, the metal oxide can be contacted with the metal salt and the organic linker substantially simultaneously to form the hydroxy double salt *in situ*.

The metal-organic framework can, for example, comprise $[\text{Cu}_3(\text{BTC})_2]$, $\text{Cu}(\text{BDC})$, $\text{Zn}(2\text{-methylimidazole})_2$, $[\text{Zn}_4\text{O}(\text{BDC-NH}_2)_3]$, $\text{Cu}(\text{ATA})$, $[\text{Zr}_6\text{O}_4(\text{OH})_4]$ (UiO-66), $[\text{Zr}_6\text{O}_4(\text{BDC-NH}_2)_6]$

(UiO-66-NH₂), or [Zr₆O₄(OH)₄(BPDC)₆] (UiO-67), where BTC represents benzene tricarboxylate, BDC represents benzene dicarboxylate, BDC-NH₂ represents aminobenzene dicarboxylate, ATA represents aminoterephthalate, and BPDC represents biphenyldicarboxylate.

The metal-organic framework can, for example, be formed in an amount of time of 15
 5 seconds or more (e.g., 20 seconds or more, 30 seconds or more, 40 seconds or more, 50 seconds or more, 1 minute or more, 2 minutes or more, 3 minutes or more, 4 minutes or more, 5 minutes or more, 10 minutes or more, 15 minutes or more, 20 minutes or more, 30 minutes or more, 40 minutes or more, 50 minutes or more, 1 hour or more, 2 hours or more, 3 hours or more, 4 hours or more, 5 hours or more, 6 hours or more, 8 hours or more, 10 hours or more, 12 hours or more,
 10 14 hours or more, 16 hours or more, 18 hours or more, 20 hours or more, or 22 hours or more).

In some examples, the metal-organic framework can be formed in an amount of time of 24 hours or less (e.g., 22 hours or less, 20 hours or less, 18 hours or less, 16 hours or less, 14 hours or less, 12 hours or less, 10 hours or less, 8 hours or less, 6 hours or less, 5 hours or less, 4 hours or less, 3 hours or less, 2 hours or less, 1 hour or less, 50 minutes or less, 40 minutes or
 15 less, 30 minutes or less, 25 minutes or less, 20 minutes or less, 15 minutes or less, 10 minutes or less, 5 minutes or less, 4 minutes or less, 3 minutes or less, 2 minutes or less, 1 minute or less, 50 seconds or less, 40 seconds or less, 30 seconds or less, 25 seconds or less, or 20 seconds or less).

The amount of time it takes to form the metal-organic framework can range from any of the minimum values described above to any of the maximum values described above. For
 20 example, the metal-organic framework can be formed in an amount of time of from 15 seconds to 24 hours (e.g., from 15 seconds to 12 hours, from 15 seconds to 6 hours, from 15 seconds to 1 hour, from 30 seconds to 30 minutes, or from 1 minute to 10 minutes).

In some examples, the method can be performed at room temperature. For example, the metal-organic framework can be formed at room temperature. As used herein room temperature
 25 means at a temperature of from 14°C to 23°C (e.g., from 14°C to 18°C, from 18°C to 23°C, or from 16°C to 21°C).

In some examples, the metal-organic framework can comprise a plurality of particles having an average particle size of 10 nm or more (e.g., 20 nm or more, 30 nm or more, 40 nm or more, 50 nm or more, 100 nm or more, 150 nm or more, 200 nm or more, 250 nm or more, 300
 30 nm or more, 400 nm or more, 500 nm or more, 600 nm or more, 700 nm or more, 800 nm or more, 900 nm or more, 1 micrometer (μm) or more, 2 μm or more, 3 μm or more, 4 μm or more, 5 μm or more, 10 μm or more, 15 μm or more, 20 μm or more, 30 μm or more, 40 μm or more, 50 μm or more, 100 μm or more, 150 μm or more, 200 μm or more, 250 μm or more, 300 μm or

more, 400 μm or more, 500 μm or more, 600 μm or more, 700 μm or more, 800 μm or more, 900 μm or more, 1 millimeter (mm) or more, 2, mm or more, 3 mm or more, 4 mm or more, 5 mm or more, 6 mm or more, 7 mm or more, 8 mm or more, or 9 mm or more).

In some examples, the metal-organic framework can comprise a plurality of particles
 5 having an average particle size of 10 mm or less (e.g., 9 mm or less, 8 mm or less, 7 mm or less, 6 mm or less, 5 mm or less, 4 mm or less, 3 mm or less, 2 mm or less, 1 mm or less, 900 μm or less, 800 μm or less, 700 μm or less, 600 μm or less, 500 μm or less, 400 μm or less, 300 μm or less, 250 μm or less, 200 μm or less, 150 μm or less, 100 μm or less, 50 μm or less, 40 μm or less, 30 μm or less, 20 μm or less, 15 μm or less, 10 μm or less, 5 μm or less, 4 μm or less, 3 μm
 10 or less, 2 μm or less, 1 μm or less, 900 nm or less, 800 nm or less, 700 nm or less, 600 nm or less, 500 nm or less, 400 nm or less, 300 nm or less, 250 nm or less, 200 nm or less, 150 nm or less, 100 nm or less, 50 nm or less, 40 nm or less, 30 nm or less, 20 nm or less, 15 nm or less, 10 nm or less, or 5 nm or less).

The average particle size of the plurality of particles comprising the metal-organic
 15 framework can range from any of the minimum values described above to any of the maximum values described above. For example, the metal-organic framework can comprise a plurality of particles having an average particle size of from 10 nm to 10 mm (e.g., from 10 nm to 5 mm, from 10 nm to 500 μm , from 50 nm to 250 μm , from 100 nm to 50 μm , from 250 nm to 10 μm , or from 400 nm to 3 μm). In some examples, the plurality of particles of the metal-organic
 20 framework can be substantially monodisperse.

The plurality of particles of the metal-organic framework can comprise particles of any shape (e.g., sphere, rod, cube, rectangle, octahedron, truncated octahedron, plate, cone, prism, ellipse, triangle, etc.). In some examples, the plurality of particles forming the metal-organic framework can have an isotropic shape. In some examples, the plurality particles forming the
 25 metal-organic framework can have an anisotropic shape. In some examples, the particles of the metal-organic framework can be crystalline.

The metal-organic framework can, for example, have an adsorption capacity for N_2 gas of 10 cm^3 of N_2 gas or more per g of metal-organic framework (e.g., 20 cm^3/g or more, 30 cm^3/g or more, 40 cm^3/g or more, 50 cm^3/g or more, 75 cm^3/g or more, 100 cm^3/g or more, 125 cm^3/g or more, 150 cm^3/g or more, 175 cm^3/g or more, 200 cm^3/g or more, 250 cm^3/g or more, 300 cm^3/g or more, 350 cm^3/g or more, 400 cm^3/g or more, 450 cm^3/g or more, 500 cm^3/g or more, or 550 cm^3/g or more). In some examples, the metal-organic framework can have an adsorption capacity for N_2 gas of 600 cm^3 of N_2 gas or less per g of metal-organic framework (e.g., 550 cm^3/g or less,
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500 cm³/g or less, 450 cm³/g or less, 400 cm³/g or less, 350 cm³/g or less, 300 cm³/g or less, 250 cm³/g or less, 200 cm³/g or less, 175 cm³/g or less, 150 cm³/g or less, 125 cm³/g or less, 100 cm³/g or less, 75 cm³/g or less, 50 cm³/g or less, 40 cm³/g or less, 30 cm³/g or less, or 20 cm³/g or less).

5 The adsorption capacity of the metal-organic framework for N₂ gas can range from any of the minimum values described above to any of the maximum values described above. For example, the metal-organic framework can have an adsorption capacity for N₂ gas of from 10 cm³ of N₂ gas per g of metal-organic framework to 600 cm³ of N₂ gas per gram of metal-organic framework (e.g., from 10 cm³/g to 300 cm³/g, from 300 cm³/g to 600 cm³/g, from 10 cm³/g to 200 cm³/g, from 200 cm³/g to 400 cm³/g, from 400 cm³/g to 600 cm³/g, or from 50 cm³/g to 550 cm³/g).

In some examples, the metal-organic framework can have an adsorption capacity for NH₃ gas of 3 moles of NH₃ gas or more per kg of metal-organic framework (e.g., 3.5 mol/kg or more, 4 mol/kg or more, 4.5 mol/kg or more, 5 mol/kg or more, 5.5 mol/kg or more, 6 mol/kg or more, 6.5 mol/kg or more, 7 mol/kg or more, or 7.5 mol/kg or more). In some examples, the metal-organic framework can have an adsorption capacity for NH₃ gas of 8 moles of NH₃ gas or less per kg of metal-organic framework (e.g., 7.5 mol/kg or less, 7 mol/kg or less, 6.5 mol/kg or less, 6 mol/kg or less, 5.5 mol/kg or less, 5 mol/kg or less, , 4.5 mol/kg or less, 4 mol/kg or less, or 3.5 mol/kg or less).

20 The adsorption capacity of the metal-organic framework for NH₃ gas can range from any of the minimum values described above to any of the maximum values described above. For example, the metal-organic framework can have an adsorption capacity for NH₃ gas of from 3 moles of NH₃ gas per kg of metal-organic framework to 8 moles of NH₃ gas per kg of metal-organic framework (e.g., from 3 mol/kg to 5.5 mol/kg, from 5.5 mol/kg to 8 mol/kg, from 3 mol/kg to 4 mol/kg, from 4 mol/kg to 5 mol/kg, from 5 mol/kg to 6 mol/kg, from 6 mol/kg to 7 mol/kg, from 7 mol/kg to 8 mol/kg, or from 4 mol/kg to 7 mol/kg).

The metal-organic framework can, for example, have an adsorption capacity for H₂S gas of 3 moles of H₂S gas per or more per kg of metal-organic framework (e.g., 3.5 mol/kg or more, 4 mol/kg or more, 4.5 mol/kg or more, 5 mol/kg or more, 5.5 mol/kg or more, 6 mol/kg or more, 6.5 mol/kg or more, 7 mol/kg or more, 7.5 mol/kg or more, 8 mol/kg or more, 8.5 mol/kg or more, 9 mol/kg or more, or 9.5 mol/kg or more). In some examples, the metal-organic framework can have an adsorption capacity for H₂S gas of 10 moles of H₂S gas or less per kg of metal-organic framework (e.g., 9.5 mol/kg or less, 9 mol/kg or less, 8.5 mol/kg or less, 8 mol/kg

or less, 7.5 mol/kg or less, 7 mol/kg or less, 6.5 mol/kg or less, 6 mol/kg or less, 5.5 mol/kg or less, 5 mol/kg or less, , 4.5 mol/kg or less, 4 mol/kg or less, or 3.5 mol/kg or less).

The adsorption capacity of the metal-organic framework for H₂S gas can range from any of the minimum values described above to any of the maximum values described above. For example, the metal-organic framework can have an adsorption capacity for H₂S gas of from 3 moles of H₂S gas per kg of metal-organic framework to 10 moles of H₂S gas per kg of metal-organic framework (e.g., from 3 mol/kg to 6.5 mol/kg, from 6.5 mol/kg to 10 mol/kg, from 3 mol/kg to 5 mol/kg, from 5 mol/kg to 7 mol/kg, from mol/kg to 10 mol/kg, or from 4 mol/kg to 9 mol/kg).

The metal-organic framework can have a BET surface area of 10 m²/g or more (e.g., 20 m²/g or more, 30 m²/g or more, 40 m²/g or more, 50 m²/g or more, 100 m²/g or more, 150 m²/g or more, 200 m²/g or more, 250 m²/g or more, 300 m²/g or more, 350 m²/g or more, 400 m²/g or more, 450 m²/g or more, 500 m²/g or more, 600 m²/g or more, 700 m²/g or more, 800 m²/g or more, 900 m²/g or more, 1000 m²/g or more, 1250 m²/g or more, 1500 m²/g or more, 1750 m²/g or more, 2000 m²/g or more, 2250 m²/g or more, 2500 m²/g or more, or 2750 m²/g or more). In some examples, the metal-organic framework can have a BET surface area of 3000 m²/g or less (e.g., 2750 m²/g or less, 2500 m²/g or less, 2250 m²/g or less, 2000 m²/g or less, 1750 m²/g or less, 1500 m²/g or less, 1250 m²/g or less, 1000 m²/g or less, 900 m²/g or less, 800 m²/g or less, 700 m²/g or less, 600 m²/g or less, 500 m²/g or less, 450 m²/g or less, 400 m²/g or less, 350 m²/g or less, 300 m²/g or less, 250 m²/g or less, 200 m²/g or less, 150 m²/g or less, 100 m²/g or less, 50 m²/g or less, 40 m²/g or less, 30 m²/g or less, or 20 m²/g or less).

The BET surface area of the metal-organic framework can range from any of the minimum values described above to any of the maximum values described above. For examples, the metal-organic framework can have a BET surface area of from 10 m²/g to 3000 m²/g (e.g., from 10 m²/g to 1500 m²/g, from 1500 m²/g to 3000 m²/g, from 10 m²/g to 1000 m²/g, from 1000 m²/g to 2000 m²/g, from 2000 m²/g to 3000 m²/g, or from 200 m²/g to 2500 m²/g).

In some examples, the metal-organic framework can have a pore volume of 0.2 cm³/g or more (e.g., 0.3 cm³/g or more, 0.4 cm³/g or more, 0.5 cm³/g or more, 0.6 cm³/g or more, 0.7 cm³/g or more, 0.8 cm³/g or more, 0.9 cm³/g or more, 1 cm³/g or more, 1.1 cm³/g or more, 1.2 cm³/g or more, 1.3 cm³/g or more, or 1.4 cm³/g or more). In some examples, the metal-organic framework can have a pore volume of 1.5 cm³/g or less (e.g., 1.4 cm³/g or less, 1.3 cm³/g or less, 1.2 cm³/g or less, 1.1 cm³/g or less, 1 cm³/g or less, 0.9 cm³/g or less, 0.8 cm³/g or less, 0.7 cm³/g or less, 0.6 cm³/g or less, 0.5 cm³/g or less, 0.4 cm³/g or less, or 0.3 cm³/g or less).

The pore volume of the metal-organic framework can range from any of the minimum values described above to any of the maximum values described above. For example, the metal-organic framework can have a pore volume of from 0.2 cm³/g to 1.5 cm³/g (e.g., from 0.2 cm³/g to 0.9 cm³/g, from 0.9 cm³/g to 1.5 cm³/g, from 0.2 cm³/g to 0.5 cm³/g, from 0.5 cm³/g to 0.8 cm³/g, from 0.8 cm³/g to 1.1 cm³/g, from 1.1 cm³/g to 1.5 cm³/g, or from 0.3 cm³/g to 1.4 cm³/g).

The methods can, for example, have a space-time-yield for forming the metal-organic framework of 1,000 kg·m⁻³·d⁻¹ or more (e.g., 2,000 kg·m⁻³·d⁻¹ or more; 3,000 kg·m⁻³·d⁻¹ or more; 4,000 kg·m⁻³·d⁻¹ or more; 5,000 kg·m⁻³·d⁻¹ or more; 6,000 kg·m⁻³·d⁻¹ or more; 7,000 kg·m⁻³·d⁻¹ or more; 8,000 kg·m⁻³·d⁻¹ or more; 9,000 kg·m⁻³·d⁻¹ or more; 10,000 kg·m⁻³·d⁻¹ or more; 12,500 kg·m⁻³·d⁻¹ or more; 15,000 kg·m⁻³·d⁻¹ or more; 17,500 kg·m⁻³·d⁻¹ or more; 20,000 kg·m⁻³·d⁻¹ or more; 22,500 kg·m⁻³·d⁻¹ or more; 25,000 kg·m⁻³·d⁻¹ or more; 27,500 kg·m⁻³·d⁻¹ or more; 30,000 kg·m⁻³·d⁻¹ or more; 32,500 kg·m⁻³·d⁻¹ or more; 35,000 kg·m⁻³·d⁻¹ or more; or 37,500 kg·m⁻³·d⁻¹ or more).

In some examples; the methods can have a space-time-yield for forming the metal-organic framework of 40,000 kg·m⁻³·d⁻¹ or less (e.g., 37,500 kg·m⁻³·d⁻¹ or less; 35,000 kg·m⁻³·d⁻¹ or less; 2,500 kg·m⁻³·d⁻¹ or less; 30,000 kg·m⁻³·d⁻¹ or less; 27,500 kg·m⁻³·d⁻¹ or less; 25,000 kg·m⁻³·d⁻¹ or less; 22,500 kg·m⁻³·d⁻¹ or less; 20,000 kg·m⁻³·d⁻¹ or less; 17,500 kg·m⁻³·d⁻¹ or less; 15,000 kg·m⁻³·d⁻¹ or less; 12,500 kg·m⁻³·d⁻¹ or less; 10,000 kg·m⁻³·d⁻¹ or less; 9,000 kg·m⁻³·d⁻¹ or less; 8,000 kg·m⁻³·d⁻¹ or less; 7,000 kg·m⁻³·d⁻¹ or less; 6,000 kg·m⁻³·d⁻¹ or less; 5,000 kg·m⁻³·d⁻¹ or less; 4,000 kg·m⁻³·d⁻¹ or less; 3,000 kg·m⁻³·d⁻¹ or less; or 2,000 kg·m⁻³·d⁻¹ or less).

The space-time-yield for forming the metal-organic framework of the methods can range from any of the minimum values described above to any of the maximum values described above. For example the methods can have a space-time-yield for forming the metal-organic framework of from 1,000 kg·m⁻³·d⁻¹ to 40,000 kg·m⁻³·d⁻¹ (e.g., from 1,000 kg·m⁻³·d⁻¹ to 20,000 kg·m⁻³·d⁻¹; from 20,000 kg·m⁻³·d⁻¹ to 40,000 kg·m⁻³·d⁻¹; from 1,000 to 10,000 kg·m⁻³·d⁻¹; from 10,000 kg·m⁻³·d⁻¹ to 20,000 kg·m⁻³·d⁻¹; from 20,000 kg·m⁻³·d⁻¹ to 30,000 kg·m⁻³·d⁻¹; from 30,000 kg·m⁻³·d⁻¹ to 40,000 kg·m⁻³·d⁻¹; or from 5,000 kg·m⁻³·d⁻¹ to 35,000 kg·m⁻³·d⁻¹).

The methods can, for example, produce the metal-organic framework in high yield. In some examples, the methods can form the metal-organic framework with a yield of 90% or more (e.g., 91% or more, 92% or more, 93% or more, 94% or more, 95% or more, 96% or more, 97% or more, 98% or more, or 99% or more).

Also disclosed herein are the metal-organic frameworks made by the methods described herein.

Also disclosed herein is a metal-organic framework comprising copper and 2-aminoterephthalate (e.g., Cu(ATA)). The Cu(ATA) metal-organic framework can have a crystal structure comprising copper paddle wheel units coordinated to the carboxylic groups in the 2-aminoterephthalate organic linker, forming a triclinic crystal structure.

5 The Cu(ATA) metal-organic framework can have a BET surface area of 28 m²/g or more (e.g., 30 m²/g or more, 35 m²/g or more, 40 m²/g or more, 45 m²/g or more, 50 m²/g or more, 55 m²/g or more, 60 m²/g or more, 65 m²/g or more, 70 m²/g or more, 75 m²/g or more, 80 m²/g or more, 85 m²/g or more, or 90 m²/g or more). In some examples the Cu(ATA) metal-organic framework can have a BET surface area of 93 m²/g or less (e.g., 90 m²/g or less, 85 m²/g or less,
10 80 m²/g or less, 75 m²/g or less, 70 m²/g or less, 65 m²/g or less, 60 m²/g or less, 55 m²/g or less, 50 m²/g or less, 45 m²/g or less, 40 m²/g or less, 35 m²/g or less, or 30 m²/g or less).

The BET surface area of the Cu(ATA) metal-organic framework can range from any of the minimum values described above to any of the maximum values described above. For example, the Cu(ATA) metal-organic framework can have a BET surface area of from 28 m²/g
15 to 93 m²/g (e.g., from 28 m²/g to 60 m²/g, from 60 m²/g to 93 m²/g, from 28 m²/g to 40 m²/g, from 40 m²/g to 55 m²/g, from 55 m²/g to 70 m²/g, from 70 m²/g to 93 m²/g, or from 35 m²/g to 90 m²/g).

The Cu(ATA) metal-organic framework can, for example, have a pore volume of 0.17 cm³/g or more (e.g., 0.2 cm³/g or more, 0.25 cm³/g or more, 0.3 cm³/g or more, 0.35 cm³/g or more,
20 0.4 cm³/g or more, 0.45 cm³/g or more, 0.5 cm³/g or more, 0.55 cm³/g or more, 0.6 cm³/g or more, 0.65 cm³/g or more, 0.7 cm³/g or more, 0.75 cm³/g or more, 0.8 cm³/g or more). In some examples, the Cu(ATA) metal-organic framework can have a pore-volume of 0.86 cm³/g or less (e.g., 0.8 cm³/g or less, 0.75 cm³/g or less, 0.7 cm³/g or less, 0.65 cm³/g or less, 0.6 cm³/g or less, 0.55 cm³/g or less, 0.5 cm³/g or less, 0.45 cm³/g or less, 0.4 cm³/g or less, 0.35 cm³/g or less,
25 0.3 cm³/g or less, 0.25 cm³/g or less, or 0.2 cm³/g or less).

The pore volume of the Cu(ATA) metal-organic framework can range from any of the minimum values described above to any of the maximum values described above. For example, the Cu(ATA) metal-organic framework can have a pore volume of from 0.17 to 0.86 cm³/g (e.g., from 0.17 cm³/g to 0.5 cm³/g, from 0.5 cm³/g to 0.86 cm³/g, from 0.17 cm³/g to 0.4 cm³/g, from
30 0.4 cm³/g to 0.6 cm³/g, from 0.6 cm³/g to 0.86 cm³/g, or from 0.25 cm³/g to 0.8 cm³/g).

The Cu(ATA) metal-organic framework can, for example, have an adsorption capacity for NH₃ gas of 2.6 moles of NH₃ gas or more per kg of Cu(ATA) metal-organic framework (e.g., 3 mol/kg or more, 3.5 mol/kg or more, 4 mol/kg or more, 4.5 mol/kg or more, 5 mol/kg or more,

5.5 mol/kg or more, 6 mol/kg or more, 6.5 mol/kg or more, 7 mol/kg or more, or 7.5 mol/kg or more). In some examples, the Cu(ATA) metal-organic framework can have an adsorption capacity for NH₃ gas of 8.2 moles of NH₃ gas or less per kg of Cu(ATA) metal-organic framework (e.g., 7.5 mol/kg or less, 7 mol/kg or less, 6.5 mol/kg or less, 6 mol/kg or less, 5.5 mol/kg or less, 5 mol/kg or less, 4.5 mol/kg or less, 4 mol/kg or less, 3.5 mol/kg or less, or 3 mol/kg or less).

The adsorption capacity for NH₃ gas of the Cu(ATA) metal-organic framework can range from any of the minimum values described above to any of the maximum values described above. For example, Cu(ATA) metal-organic framework can have an adsorption capacity for NH₃ gas of from 2.6 moles of NH₃ gas per kg of metal-organic framework to 8.2 moles of NH₃ gas per kg of metal-organic framework (e.g., from 2.6 mol/kg to 5.5 mol/kg, from 5.5 mol/kg to 8.2 mol/kg, from 2.6 mol/kg to 4 mol/kg, from 4 mol/kg to 5.5 mol/kg, from 5.5 mol/kg to 7 mol/kg, from 7 mol/kg to 8.2 mol/kg, or from 3 mol/kg to 8 mol/kg).

The Cu(ATA) metal-organic framework can, for example, have an adsorption capacity for Cl₂ gas of 0.35 moles of Cl₂ gas or more per kg of Cu(ATA) metal-organic framework (e.g., 0.4 mol/kg or more, 0.5 mol/kg or more, 0.6 mol/kg or more, 0.7 mol/kg or more, 0.8 mol/kg or more, 0.9 mol/kg or more, 1 mol/kg or more, 1.25 mol/kg or more, 1.5 mol/kg or more, 1.75 mol/kg or more, 2 mol/kg or more, 2.25 mol/kg or more, 2.5 mol/kg or more, 2.75 mol/kg or more, or 3 mol/kg or more). In some examples, the Cu(ATA) metal-organic framework can have an adsorption capacity for Cl₂ gas of 3.3 moles of Cl₂ gas or less per kg of Cu(ATA) metal-organic framework (e.g., 3 mol/kg or less, 2.75 mol/kg or less, 2.5 mol/kg or less, 2.25 mol/kg or less, 2 mol/kg or less, 1.75 mol/kg or less, 1.5 mol/kg or less, 1.25 mol/kg or less, 1 mol/kg or less, 0.9 mol/kg or less, 0.8 mol/kg or less, 0.7 mol/kg or less, 0.6 mol/kg or less, 0.5 mol/kg or less, or 0.4 mol/kg or less).

The adsorption capacity for Cl₂ gas of the Cu(ATA) metal-organic framework can range from any of the minimum values described above to any of the maximum values described above. For example, the Cu(ATA) metal-organic framework can have an adsorption capacity for Cl₂ gas of from 0.35 moles of Cl₂ gas per kg of Cu(ATA) metal-organic framework to 3.3 moles of Cl₂ gas per kg of Cu(ATA) metal-organic framework (e.g., from 0.35 mol/kg to 1.75 mol/kg, from 1.75 mol/kg to 3.3 mol/kg, from 0.35 mol/kg to 1.25 mol/kg, from 1.25 mol/kg to 2.25 mol/kg, from 2.25 mol/kg to 3.3 mol/kg, or from 0.5 mol/kg to 3 mol/kg).

In some examples, the Cu(ATA) metal-organic framework can have an adsorption capacity for NO₂ gas of 1 mole of NO₂ gas or more per kg of Cu(ATA) metal-organic framework

(e.g., 1.05 mol/kg or more, 1.1 mol/kg or more, 1.15 mol/kg or more, 1.2 mol/kg or more, 1.25 mol/kg or more, 1.3 mol/kg or more, or 1.35 mol/kg or more). In some examples, the Cu(ATA) metal-organic framework can have an adsorption capacity for NO₂ gas of 1.4 moles of NO₂ gas or less per kg of Cu(ATA) metal-organic framework (e.g., 1.35 mol/kg or less, 1.3 mol/kg or less, 1.25 mol/kg or less, 1.2 mol/kg or less, 1.15 mol/kg or less, 1.1 mol/kg or less, or 1.05 mol/kg or less).

The adsorption capacity for NO₂ gas of the Cu(ATA) metal-organic framework can range from any of the minimum values described above to any of the maximum values described above. For example, the Cu(ATA) metal-organic framework can have an adsorption capacity for NO₂ gas of from 1 moles of NO₂ gas per kg of Cu(ATA) metal-organic framework to 1.4 moles of NO₂ gas per kg of metal-organic framework (e.g., from 1 mol/kg to 1.2 mol/kg, from 1.2 mol/kg to 1.4 mol/kg, from 1 mol/kg to 1.1 mol/kg, from 1.1 mol/kg to 1.2 mol/kg, from 1.2 mol/kg to 1.3 mol/kg, from 1.3 mol/kg to 1.4 mol/kg or from 1.1 mol/kg to 1.3 mol/kg).

Also disclosed herein are methods of making the Cu(ATA) metal-organic framework. For example, the Cu(ATA) metal-organic framework can be made by any of the methods described herein.

In some examples, the methods of making the Cu(ATA) metal-organic framework can comprise contacting a metal salt with an organic linker to form a mixture; and heating the mixture at an elevated temperature for an amount of time; wherein the metal salt comprises Cu (e.g., Cu(NO₃)₂·3H₂O) and the organic linker comprises 2-aminoterephthalic acid. In some examples, the mixture can further comprise a solvent (e.g., DMF).

The elevated temperature can, for example, be 70°C or more (e.g., 75°C or more, 80°C or more, 85°C or more, 90°C or more, 95°C or more, 100°C or more, 105°C or more, 110°C or more, or 115°C or more). In some examples, the elevated temperature can be 120°C or less (e.g., 115°C or less, 110°C or less, 105°C or less, 100°C or less, 95°C or less, 90°C or less, 85°C or less, 80°C or less, or 75 °C or less). The elevated temperature can range from any of the minimum values described above to any of the maximum values described above. For example, the elevated temperature can be from 70°C to 120°C (e.g., from 70°C to 95°C, from 95°C to 120°C, from 70°C to 85°C, from 85°C to 100°C, from 100°C to 120°C, or from 80°C to 90°C).

In some examples, the amount of time can be 3 hours or more (e.g., 4 hours or more, 5 hours or more, 6 hours or more, 7 hours or more, 8 hours or more, 9 hours or more, 10 hours or more, 12 hours or more, 14 hours or more, 16 hours or more, 18 hours or more, 20 hours or more, or 22 hours or more). In some examples, the amount of time can be 24 hours or less (e.g.,

22 hours or less, 20 hours or less, 18 hours or less, 16 hours or less, 14 hours or less, 12 hours or less, 10 hours or less, 9 hours or less, 8 hours or less, 7 hours or less, 6 hours or less, 5 hours or less, or 4 hours or less). The amount of time can range from any of the minimum values described above to any of the maximum values described above. For example, the amount of time can be from 3 hours to 24 hours (e.g., from 3 hours to 14 hours, from 14 hours to 24 hours, from 3 hours to 8 hours, from 8 hours to 12 hours, from 12 hours to 16 hours, from 16 hours to 20 hours, from 20 hours to 24 hours, or from 5 hours to 20 hours).

The metal-organic frameworks described herein can be used, for example, in a variety of respiration and filter applications, for example for military and/or industrial uses for the removal of toxic gases and/or vapors. In some examples, the metal-organic frameworks can be used in gas mask filters, respirators, collective filters, etc. The metal-organic frameworks can also be used in other human protection devices, e.g., with a fabric. For example, a fabric comprising the adsorbent materials disclosed herein can be formed into protective clothing, e.g., coats, pants, suits, gloves, foot coverings, head coverings, face shields, breathing scarfs. Suitable fabrics that can be combined with the disclosed metal-organic frameworks include, but are not limited to, cotton, polyester, nylon, rayon, wool, silk, and the like.

The metal-organic frameworks can be used to remove gases and vapors (e.g., toxic gases, chemical warfare agents) from a stream of gas or liquid. These metal-organic frameworks can, for example, also be used in cleaning breathing air or exhaust gases by removing various agents. The metal-organic frameworks can remove toxic gases etc. by chemisorption and/or physisorption of the toxic gases by the metal-organic frameworks. In some examples, the metal oxide, metal salt, the hydroxy double salt, the organic linker, or a combination thereof can be chosen such that the metal-organic frameworks are effective against a range of toxic agents in a gas stream.

Also disclosed herein are filters for removing a gas from a gas stream, said filter comprising any of the metal-organic frameworks described herein. Also disclosed herein are respirators comprising any of the filters disclosed herein. Also disclosed herein are gas masks comprising any of the filters described herein. The metal-organic frameworks, filters, respirators, and/or gas masks described herein can, for example, be used for military, homeland security, first responder, civilian, and/or industrial applications.

In some examples, the metal-organic frameworks, filters, respirators, and/or gas masks can be used for the removal of a gas (e.g., a toxic industrial chemical, chemical warfare agent) from a gas stream. Examples of gases that can be removed include, but are not limited to

ammonia, chlorine, hydrogen chloride, hydrogen cyanide, cyanogen, cyanogen chloride, sulfur dioxide, hydrogen sulfide, volatile organic compounds (VOCs) (e.g., formaldehyde, ethyl acetate, glycol ethers such as ethylene glycol, acetone, chlorofluorocarbons, chlorocarbons, benzene, methylene chloride, perchloroethylene, methyl *tert*-butyl ether, toluene, xylene, styrene, naphthalene, phenol, acetaldehyde, vinyl acetate, 1,4-dioxan, dimethylformamide, epichlorohydrin), and combinations thereof.

In some examples, the metal-organic frameworks, filters, respirators, and/or gas masks can be used for the removal and degradation of a toxin (e.g., a toxic industrial chemical, chemical warfare agent). Examples of chemical warfare agents include, but are not limited to, nerve agents (e.g., sarin, soman, cyclosarin, tabun, Ethyl ({2-[bis(propan-2-yl)amino]ethyl}sulfanyl)(methyl)phosphinate (VX), *O*-pinacolylmethylphosphonofluoridate), vesicating or blistering agents (e.g., mustards, lewisite), respiratory agents (e.g., chlorine, phosgene, diphosgene), cyanides, antimiscarinic agents (e.g., anticholinergic compounds), opioid agents, lachrymatory agents (e.g., *a*-chlorotoluene, benzyl bromide, boromoacetone (BA), boromobenzylcyanide (CA), capsaicin (OC), chloracetophenone (MACE), chlormethyl chloroformate, dibenoxazepine (CR), ethyl iodoacetate, ortho-chlorobenzlidene malonitrile (CS), trichloromethyl chloroformate, xylyl bromide), and vomiting agents (e.g., adamsite (DM), diphenylchloroarsine (DA), diphenylcanoarsine (DC)). In some examples, the metal-organic frameworks, filters, respirators, and/or gas masks can be used for the removal and degradation of dimethyl 4-nitrophenyl phosphate, *O*-pinacolylmethylphosphonofluoridate, or a combination thereof.

In some examples, the half-life of the toxin on the metal-organic framework can be 10 minutes or less (e.g., 9 minutes or less, 8 minutes or less, 7 minutes or less, 6 minutes or less, 5 minutes or less, 4.5 minutes or less, 4 minutes or less, 3.5 minutes or less, 3 minutes or less, 2.5 minutes or less, 2 minutes or less, 1.5 minutes or less, or 1 minute or less).

A number of embodiments of the invention have been described. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of the invention. Accordingly, other embodiments are within the scope of the following claims.

The examples below are intended to further illustrate certain aspects of the systems and methods described herein, and are not intended to limit the scope of the claims.

EXAMPLES

The following examples are set forth below to illustrate the methods and results according to the disclosed subject matter. These examples are not intended to be inclusive of all aspects of the subject matter disclosed herein, but rather to illustrate representative methods and results. These examples are not intended to exclude equivalents and variations of the present invention which are apparent to one skilled in the art.

Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.) but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric. There are numerous variations and combinations of measurement conditions, e.g., component concentrations, temperatures, pressures and other measurement ranges and conditions that can be used to optimize the described process.

Example 1

Several strategies have been attempted to permit metal-organic framework formation at room temperature, including mechanochemical methods (Beldon PJ et al. *Angew. Chem. Int. Ed.* 2010, 49, 9640; Klimakow M et al. *Chem. Mater.* 2010, 22, 5216), irradiation-assisted synthesis (Khan NA and Jhung SH. *Bull. Korean Chem. Soc.* 2009, 30, 2921; Zou F et al. *ChemPhysChem* 2013, 14, 2825), and electrochemical approaches (WO 2005/049892 to Müller U et al.; Müller U et al. *J. Mater. Chem.* 2006, 16, 626). While these methods can reduce the reaction time and synthesis temperature for metal-organic framework production, large amounts of external energy input are required to complete the chemical reactions. Metal oxides and hydroxides have been reported to act as nucleating agents or sources of cations for room-temperature metal-organic framework synthesis (Majano G and Pérez-Ramírez J. *Adv. Mater.* 2013, 25, 1052; Zanchetta E et al. *Chem. Mater.* 2015, 27, 690). However, the incorporation of residual oxide/hydroxide seeds within the metal-organic framework crystals due to insufficient conversion can affect the purity and properties of these metal-organic frameworks. Although extending reaction time to over 1 hour (Majano G and Pérez-Ramírez J. *Adv. Mater.* 2013, 25, 1052) or increasing reaction temperature to $\geq 95^{\circ}\text{C}$ (Zanchetta E et al. *Chem. Mater.* 2015, 27, 690) can reduce the oxide/hydroxide residue in the final product, alternative approaches with relatively rapid conversion at $\sim 25^{\circ}\text{C}$ are still needed.

Herein, a synthesis method is reported that uses hydroxy double salts (HDSs) as intermediates. Hydroxy double salts are layered compounds comprising cationic sheets connected by inorganic/organic interlamellar anions (Meyn M et al. *Inorg. Chem.* 1993, 32,

1209). These materials are generally synthesized by reacting one divalent metal oxide (MO) with another different divalent cation (M^{2+}). Similar to layered double hydroxides, hydroxy double salts show anion exchangeability, and are promising for catalysis (Hara T et al. *Green Chem.* 2009, 11, 2034) and pharmaceutical applications (Bull RMR et al. *J. Mater. Chem.* 2011, 21, 1822; Taj SF et al. *Rsc Adv.* 2013, 3, 358). It was found that hydroxy double salts can undergo relatively facile conversion and can enable relatively rapid formation of metal-organic frameworks at room temperature. The space-time-yield (STY) for HKUST-1 ($Cu_3(BTC)_2$) reaches up to $3.6 \times 10^4 \text{ kg} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$, which is at least one order of magnitude greater than any prior report.

Figure 1 depicts the rapid room-temperature approach for synthesizing HKUST-1 powder. To synthesize the HKUST-1 metal-organic framework using a (Zn, Cu) hydroxy double salt intermediate, first 0.293 g of ZnO powder ($\geq 99.0\%$, Sigma-Aldrich) was dispersed in 8 mL of deionized water using sonication for 5~10 min to form the ZnO nanoslurry with an average particle size of $252 \pm 23 \text{ nm}$ (Figure 2) determined via dynamic light scattering (DLS, Zetasizer Nano, Malvern Instruments Ltd). Next, 1.74 g of $Cu(NO_3)_2 \cdot 3H_2O$ (99-104%, Sigma-Aldrich) was dissolved in 8 mL deionized water ($n(ZnO):n(Cu(NO_3)_2)=1:2$), and 0.840 g of 1,3,5-benzenetricarboxylic acid (H_3BTC , 95%, Aldrich) was separately dissolved in 16 mL ethanol (200 proof, Koptec). The $Cu(NO_3)_2$ aqueous solution and DMF were added to the ZnO nanoslurries at room temperature under magnetic stirring to form a light blue suspension of (Zn, Cu) hydroxy nitrate hydroxy double salt. The H_3BTC ethanolic solution was immediately added to the suspension under magnetic stirring, turning it turquoise in about 10 seconds. This turquoise color is a visual indication of HKUST-1 formation. After 1 minute of reaction, the powder product was immediately filtered with a polypropylene membrane filter ($0.45 \mu\text{m}$ pore size, Whatman) and washed with ethanol (50 mL, 3 times). The HKUST-1 product was dried in a fume hood for 30 min and then dried in vacuum oven ($\sim 0.01 \text{ in Hg}$) at 120°C for 6 hours. No HKUST-1 formed in the control experiments without ZnO nanoslurries.

X-ray diffraction (XRD) was conducted with a Rigaku SmartLab X-ray diffraction tool (Cu $K\alpha$ X-ray source) for crystalline phase analysis. Metal-organic framework powder diffraction patterns were also simulated using Mercury 3.0 software and the crystallographic information files from Cambridge Crystallographic Data Centre (CCDC 112954 for HKUST-1, CCDC 687690 for Cu-BDC, CCDC 175574 for IRMOF-3, and CCDC 602542 for ZIF-8).

Figure 3 compares simulated and experimental X-ray diffraction (XRD) patterns for $Cu_3(BTC)_2$ powders obtained from rapid room-temperature synthesis and 85°C solvothermal

synthesis. All peak positions match the simulated pattern, indicating the product synthesized from hydroxy double salt is crystalline HKUST-1. The metal-organic framework powder synthesized at 85°C shows a somewhat larger (111) peak, possibly a result of dehydration and rehydration. The sharp XRD peaks confirm good crystallinity of the HKUST-1.

5 Scanning electron microscopic (SEM) images were taken using a JEOL JSM 6010 SEM and an FEI Verios 460L field emission SEM. A thin layer of Au-Pd (5~10 nm) was sputter-coated onto all samples before SEM imaging. SEM images of the HKUST-1 (insert image in Figure 4 and Figure 5- Figure 6) reveal the metal-organic framework particles obtained from the rapid synthesis have an average size of $1.17 \pm 0.40 \mu\text{m}$ (Figure 7). The octahedron crystal shape
10 of the HKUST-1 is also consistent with previous observations for this fcc-type metal-organic framework crystal (Chui SSY et al. *Science* 1999, 283, 1148). After the rapid metal-organic framework synthesis, ZnO residue was not observed in SEM images (upper right panel of Figure 8) or in X-ray diffraction patterns, and no Zn was detected on the metal-organic framework surface by energy dispersive X-ray (EDX) analysis (Figure 8 and Figure 9) or by time-of-flight
15 secondary ion mass spectroscopy (ToF-SIMS) (Figure 10-Figure 13).

Energy dispersive X-ray (EDX) analysis for HKUST-1 powder was performed using an FEI Verios 460L field emission SEM equipped with an Oxford energy dispersive X-ray spectrometer. Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) analysis for HKUST-1 powder was performed using a TOF-SIMS V Instrument (ION TOF, Inc. Chestnut
20 Ridge, NY).

Inductively coupled plasma optical emission spectroscopy (ICP-OES; Perkin Elmer 8000) was also used to characterize the concentration of Cu and Zn in the metal-organic framework powder and the residue solution collected after filtration. Before ICP-OES analysis, the metal-organic framework powder was digested in a mixture of 5 mL HNO_3 , 3 mL HCl and
25 0.5 mL H_2O_2 for 1 hour using a CEM Mars 5 microwave digesting system (Gotthardt MA et al. *Dalton Trans.* 2015, 44, 2052). ICP-OES data (Table 1) reveal Zn^{2+} concentration is generally less than 0.70 wt%, demonstrating high purity within the HKUST-1 crystals.

ICP-OES analysis for the filtrate collected after synthesis of the HKUST-1 sample shows that Zn^{2+} concentration in the filtrate is at least one order of magnitude greater than that in the
30 metal-organic framework powder (HKUST-1), and that $n(\text{Zn}):n(\text{Cu})$ in the filtrate is larger than the initial molar ratio in the mixed reactants (Table 1, Table 2). These results can be explained by the conversion of ZnO to (Zn, Cu) hydroxy double salt and the release of Zn-containing species into the solution during the hydroxy double salt-to-metal-organic framework conversion.

Table 1. ICP-OES for the concentration of Cu and Zn in the HKUST-1 crystals prepared through the rapid room-temperature metal-organic framework synthesis.

$n(\text{ZnO}):n(\text{Cu}(\text{NO}_3)_2)$	Reaction Time (min)	Cu Concentration* in metal-organic framework (wt%)	Zn Concentration in metal-organic framework (wt%)	$n(\text{Zn}):n(\text{Cu})$ in metal-organic framework
1:5	1	20.9	0.034	1:628
1:3	1	28.3	0.43	1:67
2:5	1	24.2	0.40	1:62
1:2	1	29.2	0.67	1:45

*The difference of Cu concentration in the metal-organic framework is probably a result of solvent inclusion. Higher Cu concentration is observed for the samples completely activated after vacuum drying in a BET tube.

Table 2. ICP-OES for the concentration of Cu and Zn in the filtrate after collecting the HKUST-1 metal-organic framework powder by filtration.

$n(\text{ZnO}):n(\text{Cu}(\text{NO}_3)_2)$	Reaction Time (min)	Cu Concentration in filtrate* (wt%)	Zn Concentration in filtrate* (wt%)	$n(\text{Zn}):n(\text{Cu})$ in filtrate
1:3	1	14.8	6.60	1:2.3
1:2	1	11.3	9.71	1:1.2

*The solvent was further evaporated from the filtrate. While the actual concentration of Cu^{2+} and Zn^{2+} both increased during solvent removal, the ratio ($n(\text{Zn}):n(\text{Cu})$) did not change in the concentrated filtrate assuming Cu^{2+} and Zn^{2+} are not volatile.

A Quantachrome Autosorb-1C surface area and pore size analyzer was used for measuring N_2 isotherm at 77 K. Samples were dried in vacuum ($\sim 1 \times 10^{-5}$ Torr) at room temperature for 12 h before N_2 adsorption measurement. Brunauer-Emmett-Teller (BET) surface area was calculated based on the N_2 adsorption data within a relative pressure range of $P/P_0 = 0.02 \sim 0.10$ (Wong-Foy AG et al. *J. Am. Chem. Soc.* 2006, 128, 3494).

Figure 14 shows the N_2 adsorption and desorption curves for the powder prepared via rapid synthesis. The average BET surface area ($1895 \pm 84 \text{ m}^2/\text{g}$) is high compared to previous reports (Chui SSY et al. *Science* 1999, 283, 1148; Peterson GW et al. *J. Phys. Chem. C* 2009, 113, 13906; Wong-Foy AG et al. *J. Am. Chem. Soc.* 2006, 128, 3494), also suggesting the high purity of the metal-organic framework, as any residue with low surface area will reduce the overall BET surface area.

Figure 4 shows the space-time-yield (STY, in units of $\text{kg}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$) for the rapid room-temperature synthesis and the yield after 1 min of reaction. The space-time-yield (STY, in units of $\text{kg}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$) was calculated using the following equation:

$$STY = \frac{m_{MOF}}{V_{solution} \cdot \tau} \times 1.44 \times 10^6 \quad (1)$$

5 where m_{MOF} is the dry mass (g) for the metal-organic framework powder obtained from the rapid synthesis, $V_{solution}$ is the total volume (cm^3) for the mixed precursor solution, and τ is the residence time (min).

As can be seen in Figure 4, both the STY and the yield increase linearly as a function of the $n(\text{ZnO}):n(\text{Cu}(\text{NO}_3)_2)$ molar ratio ($n(\text{H}_3\text{BTC}):n(\text{Cu}(\text{NO}_3)_2)$ was kept at 1:1.8). Previous high-
 10 throughput synthesis methods for HKUST-1 show STY ranging from 225 to 1842 $\text{kg}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ (WO 2005/049892 to Müller U et al; Müller U et al. *J. Mater. Chem.* 2006, 16, 626; Majano G and Pérez-Ramírez J. *Adv. Mater.* 2013, 25, 1052). The synthesis strategy discussed herein reaches an STY up to $3.6 \times 10^4 \text{ kg}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$, an improvement of more than one order of magnitude. The yield also reaches up to 98% in just 1 minute of reaction, showing significant promise for
 15 scale-up processing. While a further increase of the $n(\text{ZnO}):n(\text{Cu}(\text{NO}_3)_2)$ ratio can lead to a higher apparent yield, a corresponding drop in the BET surface area indicates incomplete hydroxy double salt conversion due to insufficient H_3BTC reactant. By maintaining the ratio $n(\text{ZnO}):n(\text{Cu}(\text{NO}_3)_2) \leq 0.8$, all HKUST-1 samples show BET surface area exceeding 1800 m^2/g .

The hydroxy double salt can be an intermediate during the rapid room-temperature metal-
 20 organic framework synthesis, because (Zn, Cu) hydroxy nitrate hydroxy double salt can be converted from ZnO and has been reported with high reaction rate for anion exchange (Meyn M et al. *Inorg. Chem.* 1993, 32, 1209). To understand the reaction mechanism for the rapid metal-organic framework growth, how hydroxy double salt forms and how it converts to metal-organic framework were investigated.

25 Atomic layer deposition (ALD) was used to deposit ZnO thin films onto polystyrene (PS) microspheres, silicon wafers, polypropylene (PP) and polyacrylonitrile (PAN) fiber mats using a homemade hot-wall viscous-flow atomic layer deposition reactor that has been described previously (Zhao J et al. *J. Mater. Chem. A* 2015, 3, 1458). The deposition pressure was ~2 Torr, and the temperature was 100°C. In a typical ALD ZnO cycle, diethyl zinc (DEZ, 95%, STREM
 30 Chemicals) was first dosed to the reactor chamber for 2 s, followed by 60 s of N_2 (dried with an Entegris gatekeeper) purge. After DEZ dose and N_2 purge, deionized water was dosed for 2 s, and another 60 s of N_2 purge completed the ALD cycle.

Specifically, to investigate the reaction mechanism for the rapid metal-organic framework growth, ZnO thin films (34.4 ± 0.6 nm) were deposited on IR-transparent silicon wafers via atomic layer deposition (ALD) and soaked in $\text{Cu}(\text{NO}_3)_2$ aqueous solution for 1 min, followed by XRD analysis. The resulting XRD pattern (Figure 15) matches well with prior reports for (Zn, Cu) hydroxy nitrate (Meyn M et al. *Inorg. Chem.* 1993, 32, 1209). Subsequently, the hydroxy double salt was exposed to H_3BTC solution ($\text{DMF} : \text{H}_2\text{O} : \text{EtOH} = 1 : 1 : 1$ volume ratio) for 30 s, and analyzed by XRD. The XRD peaks representative for $\text{Cu}_3(\text{BTC})_2$ in the corresponding pattern and octahedron crystals found on the surface in SEM images (Figure 16 and Figure 17) confirm the formation of the targeting metal-organic framework. The decreased intensity of hydroxy double salt XRD peaks indicates hydroxy double salt is partially consumed after the short exposure to H_3BTC .

A Thermo Scientific Nicolet 6700 Fourier transform infrared (FTIR) spectrometer was used for analyzing metal-organic framework growth on IR silicon wafers. Figure 18 shows FTIR difference spectra collected for ALD ZnO thin film in the as-deposited form and after sequential exposure to $\text{Cu}(\text{NO}_3)_2$ and H_3BTC solutions. After soaking in $\text{Cu}(\text{NO}_3)_2$ aqueous solution for 1 min, the negative-going mode between 400 cm^{-1} and 480 cm^{-1} confirms loss of ZnO, and the appearance of $\nu(\text{NO}_3^-)$ (1360 cm^{-1} and 1420 cm^{-1}) and the distinct O-H group modes ($3300\text{ cm}^{-1} \sim 3620\text{ cm}^{-1}$) indicate the formation of hydroxy nitrate (Secco EA and Worth GG. *Can. J. Chem.* 1987, 65, 2504). After subsequent exposure to the H_3BTC solution for 30 s, the peaks for NO_3^- and O-H diminish while the symmetric (1378 cm^{-1}) and asymmetric (1649 cm^{-1}) stretching modes for the carboxylate groups appear. This spectrum change reveals the anion exchange process in the (Zn, Cu) hydroxy double salt, and further supports the proposed reaction path (Figure 1): ZnO reacts with $\text{Cu}(\text{NO}_3)_2$ to form (Zn, Cu) hydroxy double salt, followed by anion exchange between NO_3^- and OH^- in the hydroxy double salt and BTC^{3-} , yielding formation of HKUST-1 at room temperature.

The reactions on ZnO surface when it is exposed simultaneously to both $\text{Cu}(\text{NO}_3)_2$ and H_3BTC were also studied. ALD ZnO (58.0 ± 0.6 nm) deposited on a silicon wafer was soaked in the mixed precursor solution for 5 minutes without stirring. Cross-sections of the resulting thin films were imaged using high angle annular dark field (HAADF) scanning transmission electron microscope (STEM) (Figure 19 and Figure 20), and high-resolution EDX mapping (Figure 21) was used to analyze the elemental distribution in the cross section. The cross sections of the metal-organic framework-coated silicon wafers were prepared with an FEI Quanta 3D FEG focused ion beam (FIB), and imaged using an FEI Titan 80-300 probe aberration corrected

scanning transmission electron microscope (STEM). High-resolution EDX was analyzed using the SuperX Energy Dispersive Spectrometry (SuperX EDS) system installed on the FEI Titan STEM.

Figure 19 shows the abrupt interface between the nucleation layer and the silicon substrate, and Figure 21 indicates Zn is only present in the nucleation layer. The nucleation layer also reveals a uniformly distributed Cu signal in addition to Zn and O, further evidence for the formation of (Zn, Cu) hydroxy double salt. The C, O, and Cu signals in the metal-organic framework layer are consistent with $\text{Cu}_3(\text{BTC})_2$. These results therefore indicate that the hydroxy double salt is an important intermediate even in a one-pot batch procedure.

To demonstrate the generality of hydroxy double salt for metal-organic framework synthesis, three other metal-organic frameworks were also synthesized via hydroxy double salt intermediates. Table 3 summarizes these reaction routes. A (Zn, Zn) hydroxy acetate hydroxy double salt was formed by reacting ZnO with $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ in deionized water at room temperature for 24 h (Morioka H et al. *Inorg. Chem.* 1999, 38, 4211). ZIF-8 and IRMOF-3 were obtained from this (Zn, Zn) hydroxy double salt within 10 min at room temperature. Furthermore, (Zn, Cu) hydroxy double salt converts quickly (within 2 min) to Cu-BDC metal-organic framework. In addition to ZnO, CuO and NiO can also react with Zn^{2+} , Cu^{2+} , Ni^{2+} and Co^{2+} salts to form hydroxy double salts (Meyn M et al. *Inorg. Chem.* 1993, 32, 1209). However, most reported methods to synthesize these hydroxy double salts are slow (several days) and can require elevated temperature. Therefore, these hydroxy double salts are not desirable intermediates for rapid room temperature metal-organic framework synthesis. Important factors for analogous schemes will also include the solubility of organic linkers and the mobility of linkers in hydroxy double salt lattices. The rapid room temperature metal-organic framework synthesis of the Cu-BDC, IRMOF-3, and ZIF-8 samples are discussed in more detail below.

The synthesis of Cu-BDC metal-organic framework from a (Zn, Cu) hydroxy double salt is similar to the synthesis of the HKUST-1 sample discussed above. First, 0.293 g of ZnO powder was dispersed in 6 mL of deionized water using sonication for 5~10 min. Next, 1.74 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 6 mL deionized water ($n(\text{ZnO}):n(\text{Cu}(\text{NO}_3)_2)=1:2$), and 0.673 g of 1,4-benzenedicarboxylic acid (H_2BDC , 98%, Aldrich) was separately dissolved in 25 mL DMF. After the $\text{Cu}(\text{NO}_3)_2$ aqueous solution and H_2BDC DMF solution were prepared, the ZnO nanoslurries were mixed with 6 mL of DMF, to which the $\text{Cu}(\text{NO}_3)_2$ aqueous solution was added followed by the H_2BDC DMF solution under fast magnetic stirring. After 2 min of reaction, the turquoise powder product was immediately filtered and dried in air. Powder X-ray diffraction

(XRD) pattern for the Cu-BDC product was measured when the sample was still damp (Figure 22). As can be seen in Figure 22, the XRD pattern of the Cu-BDC obtained from hydroxy double salt agrees well with the simulated pattern and reported powder XRD patterns for this metal-organic framework (Carson CG et al. *Eur. J. Inorg. Chem.* 2009, 2009, 2338; Rodenas T et al.

5 *Nat. Mater.* 2015, 14, 48).

The powder X-ray diffraction (XRD) pattern for the product obtained by mixing (Zn, Cu) hydroxy double salt with 2-aminoterephthalic acid ($\text{H}_2\text{BDC-NH}_2$) is shown in Figure 23. The XRD pattern is similar to Cu-BDC (Figure 22), possibly corresponding to $\text{Cu}(\text{BDC-NH}_2)$. The results from the synthesis of HKUST-1 and Cu-BDC from (Zn, Cu) hydroxy double salt indicate
10 that (Zn, Cu) hydroxy nitrate is an intermediate that preferentially converts to Cu-based metal-organic frameworks.

The synthesis of the IRMOF-3 sample involved use of a (Zn, Zn) hydroxy double salt, which was synthesized at room temperature using a previously reported method (Morioka H et al. *Inorg. Chem.* 1999, 38, 4211). Specifically, 0.407 g (5 mmol) of ZnO was dispersed in 5 mL
15 of deionized water (ZnO suspension), and 1.10 g (5 mmol) of $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ ($\geq 99\%$, Sigma-Aldrich) was dissolved in 5 mL of deionized water (zinc acetate aqueous solution). The zinc acetate aqueous solution was added to the ZnO suspension under strong magnetic stirring at room temperature. After 24 hours, the mixture converted into a gel-like viscous fluid as the (Zn, Zn) hydroxy acetate hydroxy double salt formed. Next, 1.05 g of (Zn, Zn) hydroxy double salt
20 suspension was transferred to a beaker, and mixed with 25 mL of a 2-aminoterephthalic acid (0.272 g, 1.5 mmol, $\geq 99\%$, Acros Organics) DMF solution at room temperature for 10 min. The product was then filtered and dried in air. Powder XRD pattern for the IRMOF-3 product was collected when the sample was still damp (Figure 24).

The synthesis of ZIF-8 from (Zn, Zn) hydroxy double salt is similar to IRMOF-3. The
25 (Zn, Zn) hydroxy double salt was synthesized at room temperature by mixing 5 mL of ZnO aqueous suspension (1 M) with 5 mL of $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ aqueous solution (1 M) and 5 mL of DMF for 24 h. Next, 3 mL of the (Zn, Zn) hydroxy double salt suspension was added to 9 mL of a 2-methylimidazole (0.493 g, 6 mmol, 99%, Aldrich) DMF solution under fast magnetic stirring at room temperature for 10 min. The product was then filtered and dried in air. Powder XRD
30 pattern for the ZIF-8 product was collected when the sample was still damp (Figure 25).

Table 3. Routes for hydroxy double salt-Driven Room-Temperature Synthesis of Various metal-organic framework Materials

Metal Oxide	Metal Salt	Hydroxy double salt	Organic Linker	Metal-organic framework	Hydroxy double salt-to-Metal-organic framework time (min)
ZnO	Cu(NO ₃) ₂	(Zn, Cu)	Trimesic acid (H ₃ BTC)	HKUST-1 [Cu ₃ (BTC) ₂]	1
ZnO	Cu(NO ₃) ₂	(Zn, Cu)	Terephthalic acid (H ₂ BDC)	Cu-BDC [Cu(BDC)]	2
ZnO	Zn(OAc) ₂	(Zn, Zn)	2-methylimidazole (mIM)	ZIF-8 [Zn(mIM) ₂]	10
ZnO	Zn(OAc) ₂	(Zn, Zn)	2-aminoterephthalic acid (H ₂ BDC-NH ₂)	IRMOF-3 [Zn ₄ O(BDC-NH ₂) ₃]	10

The rapid room-temperature synthesis method is not limited to forming bulk metal-organic framework powders, but can also be applicable for metal-organic framework patterns and thin film coatings. For these methods, HKUST-1 precursor solutions were made by dissolving 0.870 g of Cu(NO₃)₂·3H₂O in 12 mL deionized water (*Solution A*), and dissolving 0.420 g of H₃BTC in 12 mL ethanol (*Solution B*), respectively. For reaction mechanism studies and metal-organic framework patterning, *Solution B* was mixed with equal volumes of DMF and deionized H₂O, making a H₃BTC solution (referred to as *Solution B'*) with mixed solvents (DMF:EtOH:H₂O=1:1:1). In the dip coating processes for growing metal-organic frameworks onto different substrates, 3 mL of *Solution A* was first mixed with 3 mL DMF and then 3 mL of *Solution B* in a 20 mL scintillation vial (VWR International) under mild magnetic stirring for 1 min. The mixed precursor solution (*Solution M*) was then used for growing HKUST-1 coatings on ZnO-coated substrates.

Figure 26 briefly describes the fabrication procedure for patterning HKUST-1. The negative photoresist SU-8 2050 (Microchem) was used as received and spun-coated (3000 rpm for 30 s) onto the ALD ZnO coated Si wafer. After soft baking at 65°C for 1 min and 95°C for 7 min, the wafer was exposed to a UV lamp (INTELLI-RAY 400, 60% intensity) for 5 s. The wafer was then baked at 65°C for 1 min and 95°C for 6 min, and subsequently dipped into SU-8 developer. The pre-patterned sample was rinsed in IPA and ethanol, and dried in compressed air. During metal-organic framework patterning, the sample was soaked in *Solution A* for 1 min, and

washed in ethanol for 1 min. The wafer was then transferred to *Solution B'* for 45~60 s, followed with gentle ethanol rinse for 5 min. The patterned sample was finally dried in compressed air. SEM and EDX mapping images (Figure 27) of a star-shape pattern reveal the selective HKUST-1 growth on ZnO surface. More optical micrographs of the metal-organic framework patterns are shown in Figure 28-Figure 31.

Figure 32 illustrates the general approach to grow HKUST-1 thin films onto various form factors. Taking advantage of ALD (Parsons GN et al. *MRS Bull.* 2011, 36, 865), conformal ZnO thin films can be deposited with controlled thickness on substrate materials with varied morphologies, such as polystyrene (PS) spheres, silicon wafers and polyacrylonitrile (PAN) fibers.

To synthesize HKUST-1 coatings on polystyrene spheres, 80 μ L POLYBEADTM polystyrene (PS) microspheres in aqueous suspension (3 μ m diameter, 2.5% solids in water, Polysciences Inc.) were spun-coat onto silicon wafers pretreated with O₂ plasma. The prepared sample was then coated with 200 cycles of ALD ZnO, and then dipped in *Solution M* for 1 min. The sample was then slowly lifted out of the metal-organic framework precursor solution, and carefully transferred and soaked in ethanol for 5 min. After ethanol rinsing, the samples were dried in air.

To synthesize HKUST-1 coatings on silicon wafers, 200 cycles of ALD ZnO were deposited onto silicon wafers using the above mentioned process. After ALD coating, Si wafers were soaked in *Solution M* for 1 min, and then carefully transferred to ethanol for 5 min of soaking and finally dried in air.

To synthesize HKUST-1 coatings on fibers, nonwoven polypropylene (PP) microfiber mats were used as received from the Nonwovens Cooperative Research Center (NCRC) at North Carolina State University. Electrospun polyacrylonitrile (PAN) nanofibers were used as received from RTI International. 200 cycles of ALD ZnO were deposited onto these fiber mats using the process described above. After ALD coating, the PP/ZnO and PAN/ZnO mats were soaked in the *Solution M* for 1 min and 5 min respectively, dried in air for 1 hour, and rinsed in methanol for solvent exchange for 1 day. The metal-organic framework coated fibers were finally dried at room temperature under vacuum. The XRD patterns for the metal-organic framework-coated polypropylene and polyacrylonitrile samples are shown on Figure 33 and Figure 34, respectively.

Within 1 minute of exposure to the HKUST-1 mother solution, dense coatings of HKUST-1 are also obtained on the abovementioned ZnO-coated substrates (Figure 35-Figure 37). Note that the substrate morphology is maintained with the conformal ALD ZnO thin films

(200 cycles, ~36 nm). The coatings of densely packed crystals shown in Figure 35-Figure 37 therefore solely represent the HKUST-1 metal-organic framework. More SEM and TEM images for metal-organic framework coated polystyrene spheres, polypropylene (PP) microfibers and polyacrylonitrile (PAN) nanofibers are shown in Figure 38-Figure 47.

5 Previously, it was shown that ALD Al_2O_3 promotes HKUST-1 solvothermal synthesis and layer-by-layer growth (Zhao J et al. *Adv. Mater. Interfaces* 2014, 1, 1400040; Zhao J et al. *J. Mater. Chem. A* 2015, 3, 1458). Here, using hydroxy double salt formed from ALD ZnO thin films, the synthesis time was reduced to the scale of minutes. This is also the first example showing fast fabrication of metal-organic framework-functionalized fibrous materials at room
10 temperature. By avoiding long exposure to heated organic solvents, this synthesis route can enable more metal-organic framework-based composite structures, especially for delicate substrate materials that degrade at high temperatures.

To demonstrate the functionality of these metal-organic framework-integrated materials, the adsorption capacity of metal-organic framework-coated polypropylene (PP) microfibers and
15 polyacrylonitrile (PAN) nanofibers (referred to as MOF-PP and MOF-PAN, respectively) were characterized and compared. The adsorption performance of the metal-organic framework-functionalized fiber mats was characterized with a rapid, micro-breakthrough system (Morioka H et al. *Inorg. Chem.* 1999, 38, 4211). Challenge gas (NH_3 or H_2S in moisturized air, 1000 mg/m^3 concentration, 50% relative humidity) was injected into an adsorbent column loaded with metal-
20 organic framework-fiber material (~20 mg). The column temperature was kept at 20°C in a water bath. The downstream concentration was analyzed with a continuously measuring gas chromatograph (HP5890 Series II) equipped with a photoionization detector for NH_3 or a flame photometric detector for H_2S (Glover TG et al. *Chem. Eng. Sci.* 2011, 66, 163).

BET analysis based on N_2 isotherm (Figure 48) reveals the overall surface area is 201
25 $\text{m}^2/\text{g}_{\text{MOF+Fiber}}$ and 524 $\text{m}^2/\text{g}_{\text{MOF+Fiber}}$ for the metal-organic framework-coated polypropylene microfibers (MOF-PP) and metal-organic framework-coated polyacrylonitrile nanofibers (MOF-PAN), respectively. The larger external surface area on the nanofibers enables higher metal-organic framework mass loading, leading to a larger overall BET surface area.

Breakthrough tests were also performed to quantify the performance for hazardous gas
30 removal. Dynamic loading (DL in units of mol/kg) of challenge gas on metal-organic framework-functionalized fibers was calculated using the following equations (Glover TG et al. *Chem. Eng. Sci.* 2011, 66, 163).

$$N_{feed} = \frac{C_{feed} F_{feed} \cdot t_{total}}{M_w} \quad (2)$$

$$N_{out} = \int_0^{t_{total}} \frac{C_{out} F_{feed}}{M_w} dt \quad (3)$$

$$DL = \frac{N_{feed} - N_{out}}{m_{ads}} \quad (4)$$

where N_{feed} (mol) is the total moles of challenge gas injected into the adsorbent column, N_{out} (mol) is the total moles of challenge gas detected in the downstream. C_{feed} and C_{out} (g/m³) are the concentrations of challenge gas in the feed and the downstream respectively. F_{feed} (m³/min) is the feed flow rate, t (min) is test time. M_w (g/mol) is the molecular weight of the challenge gas, and m_{ads} (kg) is the adsorbent mass.

Figure 49 compares the NH₃ dynamic loadings on polypropylene and polyacrylonitrile fiber mats with and without metal-organic framework coatings. Untreated polypropylene and polyacrylonitrile fibers can barely retain the NH₃ challenge gas, while the metal-organic framework-coated polypropylene microfibers (MOF-PP) and metal-organic framework-coated polyacrylonitrile nanofibers (MOF-PAN) exhibit 36× and 18× higher dynamic loadings towards ammonia than the corresponding untreated fibers. In addition to NH₃, the metal-organic framework-functionalized fibers also show high adsorption capacity for H₂S (Figure 50-Figure 52), another highly toxic industrial chemical. These results all suggest the fibrous materials with metal-organic framework coatings are promising for gas filtration and protective garments.

In summary, a fast room-temperature metal-organic framework synthesis strategy using hydroxy double salt intermediates was discussed. The (Zn, Cu) hydroxy double salt intermediate formed *in situ* from ZnO particles or thin films shows a high rate of anion exchange in the linker solution and drives the rapid formation (< 1 min) of HKUST-1 (Cu₃(BTC)₂) at room temperature. The space-time-yield for HKUST-1 reaches 3.6×10^4 kg·m⁻³·d⁻¹, which is at least one order of magnitude higher than previous published reports. The high anion exchange rate of (Zn, Cu) hydroxy nitrate hydroxy double salt drives the ultra-fast metal-organic framework formation. Similar synthetic strategies using hydroxy double salts were used to obtain Cu-BDC, ZIF-8 and IRMOF-3, demonstrating the synthetic generality. Using ZnO thin films deposited via atomic layer deposition (ALD), metal-organic framework patterns are obtained on pre-patterned surfaces, and dense HKUST-1 coatings are grown onto various form factors including polystyrene microspheres, silicon wafers, and polypropylene and polyacrylonitrile fiber mats were obtained in a fast processing rate at room temperature. Breakthrough tests show the metal-

organic framework-functionalized fibers have high adsorption capacity for toxic gases. The hydroxy double salt-driven metal-organic framework synthesis approach reported here can improve metal-organic framework production rates and can expand the material set of metal-organic framework-functionalized composites.

5

Example 2

Amino-functionalized metal-organic frameworks (MOFs) can exhibit large adsorption capacity and excellent separation performance for CO₂, enhanced catalytic and photo-catalytic properties, and amenability for post-synthetic modification due to the -NH₂ groups on the organic linker. There is no Cu-based metal-organic framework reported with 2-aminoterephthalic acid (H₂ATA) linkers to date.

Herein, a metal-organic framework comprising Cu-Cu paddle wheels and ATA²⁻ bridging ligands is discussed. This metal-organic framework can be synthesized using two different methods. For conventional solvothermal method, 1.053 g of Cu(NO₃)₂·3H₂O and 0.789 g of H₂ATA were dissolved in 87 mL of *N,N*-dimethylformamide (DMF) and heated at 85°C for 24 h.

The second method is a rapid synthesis technique similar to that discussed above in Example 1 for Cu-BTC and Cu(BDC). It was also found that (Zn, Cu) hydroxy double salt formed from ZnO can generate Cu(ATA) within 2 min. Specifically, 0.293 g of ZnO was first dispersed in 8 mL of deionized water, and 1.74 g of Cu(NO₃)₂·3H₂O was dissolved in 8 mL of deionized water. The ZnO aqueous suspension was then mixed with 8 mL of DMF and the Cu(NO₃)₂ solution. Next, 25 mL of H₂ATA (0.734 g, 0.162 M) DMF solution was added to the mixed solution, and the reaction proceeded for 2 min. Cu(ATA) powder was filtered and washed with ethanol after synthesis and further activated in vacuum with moderate heating (110°C).

Figure 53 illustrates the crystal structure for the copper 2-aminoterephthalate [Cu(ATA)] metal-organic framework. Similar to the crystal structure for Cu(BDC), copper paddle wheel units are coordinated to the carboxylic groups in the ATA²⁻ linker, forming a triclinic crystal structure (space group P 1, with $a = 11.2991 \text{ \AA}$, $b = 14.9485 \text{ \AA}$, $c = 8.0480 \text{ \AA}$, $\alpha = 90.1963^\circ$, $\beta = 111.9833^\circ$, $\gamma = 89.7384^\circ$, $V = 1260.5 \text{ \AA}^3$) (Mori W et al. *Chem. Lett.* 1997, 26 (12), 1219–1220; Carson CG et al. *Eur. J. Inorg. Chem.* 2009, 2009 (16), 2338–2343; Rodenas T et al. *Nat. Mater.* 2015, 14 (1), 48–55).

Figure 54 shows the powder X-ray diffraction (XRD) pattern of Cu(ATA). Materials Studio 7.0 was used to modify the crystallographic information for Cu(BDC) (CCDC-687690)

by changing the monoclinic space group ($C2/m$) with triclinic $P1$ space group and adding $-NH_2$ functionality to the benzene ring of the terephthalate linkers (all hydrogens on the BDC^{2-} linker were replaced with $-NH_2$ for symmetry). The Cu(ATA) crystal structure was further refined using Rietveld refinement in GSAS-II software.

Figure 55 shows the N_2 isotherm for Cu(ATA) measured at 77 K. Compared to common Type-I isotherm, this metal-organic framework exhibits a Type-III isotherm, indicating weak adsorbate-adsorbent interaction. The BET surface area calculated from the isotherm ($P/P_0 = 0.02 - 0.10$) is $92.85 \text{ m}^2/\text{g}$, and the total pore volume is $0.863 \text{ cm}^3/\text{g}$. The surface area of Cu(ATA) is lower than Cu(BDC), possibly because the strong hydrogen bonding between the layered structures due to the amino-functionality. The adsorbed N_2 volume increases dramatically at high relative pressure regime, indicating a possible expansion of the crystal structure, since similar MIL-53 structures have flexible breathing effect during gas adsorption (Serre C et al. *J. Am. Chem. Soc.* 2002, 124 (45), 13519–13526; Chen L et al. *J. Am. Chem. Soc.* 2013, 135 (42), 15763–15773).

Figure 56 is the attenuated total reflectance infrared (ATR-IR) spectrum for Cu(ATA). The presence of N-H stretching modes (3363 cm^{-1} and 3477 cm^{-1}) and the symmetric stretching mode for carboxylate groups confirm the formation of aminoterephthalate.

The morphology of Cu(ATA) powder was also investigated using scanning electron microscopy (SEM). Figure 57 shows an SEM image of Cu(ATA) particles. Layered structures of stacked 2D nanosheets were observed for this metal-organic framework, consistent with the refined crystal structure based on XRD results.

The adsorptive capacity of Cu(ATA) was investigated for a variety of toxic industrial chemicals (TICs), and found that this metal-organic framework is promising for removing several toxic industrial chemicals including NH_3 , Cl_2 and NO_2 . Micro-breakthrough analysis was performed to determine the adsorption capacities of Cu(ATA) for toxic industrial chemicals. Figure 58 and Figure 59 show breakthrough curves for NH_3 and Cl_2 , respectively. When tested at humid condition, Cu(ATA) exhibits a dynamic loading of NH_3 up to 8.2 mol/kg . This value is very high, compared other common metal-organic frameworks (Britt D et al. *Proc. Natl. Acad. Sci. U. S. A.* 2008, 105 (33), 11623–11627). Cu(ATA) also shows a large adsorption capacity for Cl_2 (up to 3.3 mol/kg measured at dry conditions). Furthermore, this metal-organic framework also shows large dynamic loading for NO_2 , indicating that Cu(ATA) is promising for broad-spectrum toxic industrial chemical protection.

In conclusion, an amino-functionalized metal-organic framework with copper metal units [Cu(ATA)] was synthesized. The crystal structure of the Cu(ATA) metal-organic framework was refined based on the powder XRD pattern, and this metal-organic framework was characterized with BET, ATR-IR and SEM. Micro-breakthrough analysis revealed that this Cu(ATA) metal-organic framework was able to remove toxic industrial chemicals. This metal-organic framework could provide broad-spectrum protection for toxic industrial chemicals and can be used for the next generation of gas filters.

Example 3

Chemical warfare agents (CWAs) are highly toxic compounds that can injure, incapacitate, or even kill human beings. Detoxification of chemical warfare agents is of great social significance owing to the past accidental or deliberate emissions and remaining threat posed to civilian and military personnel. Materials that can efficiently capture and degrade these lethal chemicals are therefore highly desired to protect soldiers, first-responders, and the general public. The threat associated with chemical warfare agents motivates the development of new materials to provide enhanced protection with a reduced burden.

A wide variety of materials have been reported with catalytic activity for degrading chemical warfare agents. Metal-organic frameworks (MOFs) have been shown as highly effective adsorbents and catalysts for removing chemical warfare agents. The high surface area and large porosity make metal-organic frameworks promising candidates for sorption of chemical warfare agents, while the metal-containing secondary building units present in metal-organic frameworks can also function as Lewis-acidic catalytic sites for chemical warfare agent destruction.

While bulk metal-organic framework crystals exhibit excellent properties for chemical warfare agent destruction, many practical issues still need to be addressed before these materials can be widely used for this application. For example, the powder form of metal-organic frameworks is not the ideal configuration for gas filters, protective suits and clothing. Additionally, particle aggregation may lead to reduced accessible catalytic sites and consequently decreased activity. Minimizing the volume and weight of the active materials is important for reducing the burden for end users while maintaining substantial long-term protection. In contrast, metal-organic framework thin films immobilized on functional substrates can simplify the handling and deployment.

Herein, a series of metal-organic framework–nanofiber kebab structures for chemical warfare agent degradation are discussed. Electrospun polymeric nanofibers were chosen as the scaffolds because such nanofibers can exhibit high external surface area, excellent water vapor transport properties, and good mechanical strength. Conformal, high-quality metal-organic framework thin-films grown on the nanofibers are explored for catalytic destruction of chemical warfare agents. Herein, the half-lives of the nerve agent soman (*O*-pinacolyl methylphosphonofluoridate, also known as GD) is as short as 2.3 min using the metal-organic framework–nanofiber composite catalysts described herein. This is the first demonstration of effective destruction of a real chemical warfare agent compound using metal-organic framework–fabric composites.

Experimental

Synthesis of Zr-based metal-organic frameworks. Three Zr-based metal-organic frameworks (UiO-66, UiO-66-NH₂ and UiO-67) were synthesized using slightly modified recipes based on previous reports (Schaate A et al. *Chem. – Eur. J.* **2011**, *17*, 6643; Katz MJ et al. *Chem. Commun.* **2013**, *49*, 9449).

For the solvothermal synthesis of UiO-66, 0.080 g (0.343 mmol) of ZrCl₄ ($\geq 99.5\%$, Alfa Aesar) was added to 20 mL of DMF (Fisher) in a glass scintillation vial, followed with 1 min of sonication and 5 min of magnetic stirring to dissolve the ZrCl₄. Next, 0.057 g (0.0343 mmol) of benzene-1,4-dicarboxylic acid (H₂BDC, 98%, Sigma) was added to the ZrCl₄ solution under stirring. Subsequently, 25 μ L of deionized water and 1.33 mL of concentrated hydrochloric acid (NF/FCC grade, Fisher) were added to the mixed solution. The vial was then placed in a box furnace (Thermo Scientific) and heated to 85°C for 24 h.

After the solvothermal synthesis, the UiO-66 powder product was filtered using a polypropylene membrane (0.45 μ m pore size, Whatman) and washed with DMF twice. Anhydrous ethanol (200 proof, VWR) was used for solvent exchange, and the solvent was replaced every 24 h for a total of two times. After solvent exchange, the UiO-66 powder was collected via filtration and dried in a dessicator at room temperature at reduced pressure for 12 h. To further activate the metal-organic framework, ~ 0.3 g of powder product dried in BET at 80°C for 12 hour and then at 110 °C for 12~18 h (heating temperature was slowly ramped from 80°C to 110°C).

For UiO-66-NH₂, the recipe and synthesis procedure are similar to UiO-66, except 0.062 g (0.343 mmol) of 2-aminoterephthalic acid (H₂BDC-NH₂, 99%, Sigma) was used as the organic

linker instead of H₂BDC. The amounts of ZrCl₄, DMF, H₂O and HCl were kept same as UiO-66. Reaction temperature was controlled at 85 °C for 24 h. After synthesis, the washing step, solvent exchange and drying process for UiO-66-NH₂ were similar to UiO-66.

For UiO-67, 0.083 g (0.343 mmol) of biphenyl-4,4'-dicarboxylic acid (H₂BPDC, 97%, Sigma) was used as the ligand. The same amounts of ZrCl₄, DMF, H₂O were used as UiO-66. The addition of the HCl modulator was reduced to 0.67 mL for 20 mL of mixed solution. The reaction proceeded at 85 °C for 24 h. After synthesis, the washing step, solvent exchange and drying process for UiO-66-NH₂ were similar to UiO-66.

Electrospinning of Polyamide-6 Nanofiber Mat. Polyamide-6 (referred to as PA-6, Scientific Polymer Products) was dissolved overnight in a solvent mixture of glacial acetic acid (Sigma Aldrich) and formic acid (spectroscopy grade, Fluka) (glacial acetic acid:formic acid = 2 : 1 wt/wt) to reach a final PA-6 concentration of 12 wt%. The polymer solution was then loaded into a syringe with a 27 gauge stainless steel needle attached and placed into a custom-built electrospinning system described previously (US Patent 7,297,305). An atmosphere of bone dry grade carbon dioxide gas (Airgas) was mixed with water vapor to form ~50% relative humidity (RH) at an ambient temperature of ~22°C. This RH controlled, CO₂ atmosphere provides a stable environment for electrospinning the fibers. The spinning conditions were a voltage gradient of 1.57 kV/cm, a 25 cm spinning distance (needle to collection substrate distance), and 90 minutes elapsed spinning time. The polymer solution was continuously fed through the needle at a rate to maintain a stable electrospinning jet. PA-6 nanofibers were deposited onto a paper ring (10 cm outside diameter and 6.5 cm inside diameter) sitting on a 3.5-inch (~8.9 cm) petri dish filled with deionized water. The water provided a collection surface for the forming fibers during electrospinning. After electrospinning the paper ring with the nanofiber mat deposited thereon was carefully removed and dried overnight at ambient conditions.

Atomic Layer Deposition of TiO₂ on PA-6 Nanofibers. A thin film of TiO₂ was deposited onto free-standing PA-6 nanofiber mat using atomic layer deposition (ALD) before growing Zr-based metal-organic framework coatings. A custom-built hot-wall viscous-flow reactor that has been described previously was used for ALD TiO₂ processes (Zhao J et al. *J. Mater. Chem. A* **2015**, 3, 1458). In a typical ALD TiO₂ cycle, titanium (IV) chloride (TiCl₄, 99%, STREM Chemicals) was first dosed to the reactor chamber for 1 s, followed with 40 s of N₂ (99.999%, Airgas, further purified with an Entegris gatekeeper). After the TiCl₄ dose and N₂ purge, deionized H₂O was dosed to the chamber for 1 s, and the chamber was subsequently purged with N₂ for 60 s. The process temperature was controlled at 100°C, and the pressure was about 1.3

Torr. All PA-6 nanofibers were coated with 100 cycles of ALD TiO₂ before solvothermal metal-organic framework growth.

Synthesis of Zr-based metal-organic framework Coatings on Nanofibers. Precursor solutions for Zr-based metal-organic framework coatings (e.g., UiO-66, UiO-66-NH₂ and UiO-67) were prepared using the recipe and procedure described above for Zr-based metal-organic framework powders. Approximately, 10 mg of free standing PA-6 nanofiber mat coated with ALD TiO₂ was transferred into a 20 mL scintillation vial and soaked in the metal-organic framework precursor solution. The vial was then placed in a box furnace and heated at 85°C for 24 h. After the solvothermal synthesis, the metal-organic framework-coated PA-6 nanofiber mat was transferred into a fine aluminum mesh and washed with 100 mL of DMF twice. After DMF wash, the metal-organic framework-coated nanofiber mat was further exchanged in anhydrous ethanol, and the solvent was replaced every 12 h for a total of three times. To fully activate the metal-organic framework coating, the metal-organic framework-coated nanofiber mat was first dried in a dessicator at room temperature at reduced pressure for 12 h, and then in a BET at 80°C for 12 hours and subsequently at 110°C for 12~18 h (heating temperature was slowly increased from 80 °C to 110 °C).

Synthesis of UiO-66-NH₂ Thin Films on Si Wafers. 300 cycles of ALD TiO₂ were deposited onto Si wafer using the same process described above for PA-6 nanofibers. A precursor solution for UiO-66-NH₂ was prepared using the abovementioned recipe for UiO-66-NH₂ powders. The ALD-TiO₂ coated Si wafer was placed horizontally (with polished side facing down) in a Teflon sample holder and then transferred to the solvothermal precursor solution in a Teflon-lined autoclave (Parr Instrument Co.). The autoclave was then placed in a box furnace (Thermo Scientific) and heated at 85°C for 24 h.

Material Characterization. Scanning electron microscopy (SEM) images were obtained using an FEI Verios 460L field emission SEM. All samples were sputter-coated with Au-Pd (5~10 nm) before imaging. Energy dispersive X-ray (EDX) mapping images was taken using an Oxford energy dispersive X-ray spectrometer attached to the FEI Verios 460L FESEM. Cross sections of the metal-organic framework-coated nanofibers were obtained via microtoming, and imaged using a JEOL 2010F field emission transmission electron microscope (TEM). X-ray diffraction (XRD) was performed using a Rigaku SmartLab X-ray diffraction tool (Cu K α X-ray source) for crystalline phase analysis. A glass sample holder was used for powder samples, and an aluminum holder was used for nanofiber samples. Powder diffraction patterns for the Zr-based metal-organic frameworks were also simulated using Mercury 3.0 software based on the

crystallographic information files from Cambridge Crystallographic Data Centre (CCDC 733458 for UiO-66, CCDC 733458 for UiO-67, no CIF available for UiO-66-NH₂). BET surface area of metal-organic framework powders was measured with a Micromeritics ASAP 2020 surface area and porosimetry analyzer, and metal-organic framework-coated nanofiber samples were
5 analyzed using a Quantachrome Autosorb-1C surface area and pore size analyzer. Samples were dried in vacuum at 80°C for 12 hour and subsequently at 110°C for 12~18 h (heating temperature was slowly increased from 80°C to 110°C) before N₂ adsorption measurement. BET surface area was calculated based on the N₂ adsorption data within a relative pressure range of $P/P_0 = 0.02 \sim 0.07$ (this range meets the criteria for determining BET surface area of
10 microporous materials described in literature) (Walton KS and Snurr RQ. *J. Am. Chem. Soc.* **2007**, *129*, 8552; Thommes M et al. *Pure Appl. Chem.* **2015**, *87*, 1051).

The cross sections of the UiO-66-NH₂ thin film on Si wafers were prepared using an FEI Quanta 3D FEG focused ion beam (FIB) equipped with a micromanipulator. Cross-sectional TEM images were taken using an FEI Titan 80-300 probe aberration corrected scanning
15 transmission electron microscope (STEM). High-resolution EDX mapping images were obtained using a SuperX Energy Dispersive Spectrometry (SuperX EDS) system installed on the FEI Titan STEM. Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) analysis for the UiO-66-NH₂ thin film on Si wafers was performed using a TOF-SIMS V Instrument (ION TOF, Inc. Chestnut Ridge, NY). Perkin Elmer Elan DRCII Inductively-coupled plasma-mass
20 spectroscopy (ICP-MS) was used for analyzing the concentration of Zr and Ti in the crude dimethyl 4-nitrophenyl phosphate (DMNP) reaction mixture.

Degradation of Dimethyl 4-Nitrophenyl Phosphate (DMNP). The kinetics of catalytic degradation of dimethyl 4-nitrophenyl phosphate (DMNP) was characterized using a procedure similar to the methods described in previous reports (Katz MJ et al. *Angew. Chem. Int. Ed Engl.*
25 **2014**, *53*, 497; Mondloch JE et al. *Nat. Mater.* **2015**, *14*, 512). Specifically, 2.5 mg of metal-organic framework powder sample or 14 mg of metal-organic framework-coated nanofiber sample was first dispersed in 1 mL of *N*-ethylmorpholine aqueous solution (0.45 M) in a 2 mL Eppendorf tube under fast magnetic stirring (1100 rpm stir rate set on a Thermo Scientific stir plate) for 20 min. DMNP (4 μ L, ~5.6 mg, 0.023 mmol) was then added to the metal-organic
30 framework suspension. The Eppendorf tube was kept on the stir plate (1100 rpm stir rate) during the reaction. A 20 μ L aliquot was taken from the reaction mixture each time and diluted in 10 mL of *N*-ethylmorpholine aqueous solution (0.15 M) for UV-visible absorbance spectroscopy. The reaction progress was evaluated by monitoring the *p*-nitrophenoxide (degraded product from

DMNP) absorbance at 407 nm. The concentration of *p*-nitrophenoxide was calculated based on Lambert-Beer Law (Equation 5).

$$A = -\log \frac{I}{I_0} = \varepsilon Cl \quad (5)$$

where A is the absorbance in units of absorbance unit (a.u.), I_0 is the incident light intensity, I is the transmitted light intensity, ε is the molar absorptivity coefficient ($\varepsilon = 18330 \text{ M}^{-1}\text{cm}^{-1}$), C is the analyte concentration in units of M, l is the length of light path in units of cm.

The percent conversion of DMNP was obtained from the ratio of the *p*-nitrophenoxide concentration before dilution to the initial DMNP concentration in the reaction mixture.

To test the heterogeneity of the catalytic reaction, PA-6@TiO₂@UiO-66-NH₂ was removed from the crude reaction mixture after 5 minutes using a 3-mL plastic syringe and Millipore 0.22- μm filter. The filtrate was collected in a 2-mL Eppendorf tube, and kept stirring until the reaction time reached 1 hour. The conversion of DMNP after the catalyst was removed was measured using the same method as mentioned above.

For the cycle test, the metal-organic framework-nanofibers were collected via filtration and washed with pure ethanol three times. After soaking the metal-organic framework nanofibers in ethanol for 1 hour, these materials were transferred into a BET tube and vacuum dried in BET for 10 hours at room temperature. After the samples were activated in BET, they were weighed and added to a 2 mL Eppendorf tube for the next cycle of DMNP test.

Degradation of O-Pinacolyl Methylphosphonofluoridate (GD). Approximately 14 mg of metal-organic framework-coated PA-6@TiO₂ nanofibers was weighed on a Mettler Toledo AB104 calibrated digital scale. Once weighed, the samples were placed into a humidity chamber (Thunder Scientific Corporation Series 2500) at 25°C to condition them at 50% relative humidity (RH) for at least 16 h. Upon humidification completion, the samples were transferred into a 4-mm glass NMR tube. Deionized water (700 μL) and 47 μL of *N*-ethylmorpholine (buffer) were then added to the NMR tube. After 2.6 μL of *O*-pinacolylmethylphosphonofluoridate (GD) was added onto the inner wall of the NMR tube, the tube was capped and vigorously shaken in order to ensure mixture of GD with metal-organic framework-nanofibers in the solution. The time of solution agitation was recorded in order to account for the Δt of mix time vs initial scan time. ³¹P NMR spectra were obtained over time at ambient temperature (24-25°C) using a Varian INOVA 400 NB NMR spectrometer equipped with a Doty Scientific 4-mm Liquid NMR probe to monitor the reaction and to identify the products. The samples were not spun in order to limit slurry formation and obtain good reproducibility. Samples scan times employed a 90° pulse widths of 4 μs and an overall acquisition time of 8 min per acquisition. The half-lives of GD in

the reactions without *N*-ethylmorpholine buffer exceed 300 min. Under same reaction conditions, the half-lives of GD are less than 4 min with the presence of *N*-ethylmorpholine. The HF formed during the reaction likely poisons the active sites on the metal-organic framework coatings, while the *N*-ethylmorpholine buffer can neutralize HF and maintain the catalytic properties of the metal-organic frameworks.

The following equation can correlate the metal-organic framework mass fraction with the overall BET surface per unit mass of metal-organic framework plus fibers (Equation 6):

$$SA_{MOF} \approx \frac{SA_{MOF+fiber} \times m_{MOF+fiber} - SA_{fiber} \times m_{fiber}}{m_{MOF+fiber} - m_{fiber}} \quad (6)$$

where m is the mass and SA is the surface area for each component (Zhao J et al. *Adv. Mater. Interfaces* **2014**, 1400040).

With known surface area for the uncoated fiber substrate, the metal-organic framework-coated fibers and the bulk metal-organic framework material, the metal-organic framework mass fraction (ω) can be calculated using Equation 7 or Equation 8:

$$SA_{MOF+fiber} = SA_{MOF} \cdot \omega + SA_{fiber} \cdot (1 - \omega) \quad (7)$$

or

$$\omega = \frac{SA_{MOF+fiber} - SA_{fiber}}{SA_{MOF} - SA_{fiber}} \quad (8)$$

The metal-organic framework weight percentage calculated in this approach is similar to what was measured by the ICP-OES method. This method provides a simple and straightforward way to calculate the metal-organic framework weight percent when instruments for elemental analysis are not available. One prerequisite is that both the metal-organic framework coatings on the fibers and the bulk metal-organic framework powder are fully activated for BET measurements. It is also recommended to use the metal-organic framework crystals collected from the same batch for metal-organic framework synthesis on fibers for BET analysis in order to obtain a more accurate metal-organic framework mass fraction.

Results and Discussion

Figure 60 describes the procedure to synthesize the metal-organic framework–nanofiber kebab structures. Free-standing polyamide-6 (PA-6) nanofiber mats obtained from electrospinning were coated with a conformal thin-layer (~ 5 nm thick) of TiO₂ using atomic layer deposition (ALD). This TiO₂ ALD layer can promote metal-organic framework heterogeneous nucleation on fibers (Zhao J et al. *Adv. Mater. Interfaces* **2014**, 1, 1400040), and can provide some contribution to catalytic chemical warfare agent detoxification (Wagner GW et al. *J. Phys. Chem. C* **2008**, 112, 11901; Wagner GW et al. *Ind. Eng. Chem. Res.* **2012**, 51, 3598). Although previous work has shown that Al₂O₃ and ZnO ALD can also promote metal-organic

framework growth on fibers (Zhao J et al. *Adv. Mater. Interfaces* **2014**, *1*, 1400040; Zhao J et al. *J. Am. Chem. Soc.* **2015**, *137*, 13756; Lemaire PC et al. *ACS Appl. Mater. Interfaces* **2016**, *8*, 9514), these ALD films were not used as nucleation layers in this case due to substrate incompatibility with the Al₂O₃ ALD process and instability of ZnO in the highly acidic solvothermal solution used.

Three Zr-based metal-organic frameworks, including UiO-66, UiO-66-NH₂, and UiO-67, were chosen because they have excellent stability and good catalytic properties (Katz MJ et al. *Angew. Chem. Int. Ed.* **2014**, *53*, 49; Moon SY et al. *Angew. Chem. Int. Ed.* **2015**, *54*, 6795; Peterson GW et al. *Inorg. Chem.* **2015**, *54*, 9684; Cavka JH et al. *J. Am. Chem. Soc.* **2008**, *130*, 13850). Concentrated HCl was used as the modulator for the solvothermal synthesis, which is similar to reported recipes for these metal-organic frameworks (Katz MJ et al. *Chem. Commun.* **2013**, *49*, 9449), but modified to achieve optimized growth of metal-organic framework thin-films on the nanofiber substrates. Specifically, 0.343 mmol of ZrCl₄ and 0.343 mmol of dicarboxylic acid linkers (1:1 molar ratio) were dissolved in 20 mL of DMF. Deionized water (25 mL) and concentrated HCl (1.33 mL for UiO-66 and UiO-66-NH₂, 0.67 mL for UiO-67) were added to the solution. Subsequently, the TiO₂-coated PA-6 nanofiber (PA-6@TiO₂) mat was transferred into the mixed solution, which was then heated at 85°C for 24 h. After the solvothermal synthesis, the metal-organic framework–nanofiber kebabs were collected, washed, activated, and investigated for chemical warfare agent degradation.

Figure 61a is a photo of a free-standing PA-6@TiO₂ nanofiber mat coated with UiO-66-NH₂ metal-organic framework kebabs (referred to as PA-6@TiO₂@UiO-66-NH₂). The structural integrity and flexibility were fully maintained after the solvothermal synthesis. SEM images (Figure 61b–Figure 61d) show that UiO-66-NH₂ crystals (average size = 126 ± 25 nm) were grown conformally on the PA-6@TiO₂ nanofibers. The method reported here enables the formation of these metal-organic framework–nanofiber kebab structures. In contrast, the growth of UiO-66-NH₂ on PA-6 nanofibers without TiO₂ nucleation layers is patchy and does not result in a conformal thin-film on the nanofiber surface as that on TiO₂-coated PA-6 nanofibers using the same synthesis conditions (Figure 62a–Figure 62d). Energy dispersive X-ray analysis (Figure 61e–Figure 61i) also confirmed uniform metal-organic framework growth on the nanofibers.

In addition to UiO-66-NH₂, kebab structures of UiO-66 and UiO-67 were also obtained on PA-6@TiO₂ nanofibers (referred to as PA-6@TiO₂@UiO-66 and PA-6@TiO₂@UiO-67, respectively). Figure 63a–Figure 63f are SEM and cross-sectional TEM images of the metal-organic framework–nanofiber kebabs. Tubular features observed in the TEM images represent

the core@shell structures of PA-6@TiO₂ nanofibers sliced along the axial direction. The diameters of PA-6 nanofibers measured from TEM images (15–55 nm) are consistent with that measured from SEM images (Figure 64a–Figure 64d). The average thickness of the ALD TiO₂ coatings is 5.7 ± 1.3 nm, corresponding to an ALD growth rate of ~ 0.6 Å per cycle. The spherical metal-organic framework crystals are found to nucleate and grow directly on and around the PA-6@TiO₂ nanofibers, indicating strong attachment to the substrates. There was no noticeable particle shedding during the handling after synthesis, confirming good adhesion of the metal-organic framework coatings to the nanofibers.

The quality of the Zr-based metal-organic framework thin-films grown on nanofibers was characterized using XRD and BET. The sharp XRD peaks in the patterns for the metal-organic framework–nanofiber kebabs agree well with the corresponding metal-organic framework powders (Figure 65a–Figure 65c), confirming the formation of targeted metal-organic framework structures. N₂ physisorption measurements (Figure 65d–Figure 65f) reveal that the BET surface area is $143.9 \text{ m}^2 \text{ g}^{-1}$, $205.9 \text{ m}^2 \text{ g}^{-1}$, and $356.2 \text{ m}^2 \text{ g}^{-1}$ for the metal-organic framework–nanofiber kebabs with UiO-66, UiO-66-NH₂ and UiO-67, respectively (Table 4). The surface area for the metal-organic framework–nanofiber kebabs is in excess of 10-times larger than the nanofiber scaffolds alone, demonstrating the high porosity of the metal-organic framework coatings. The surface area of the UiO-type metal-organic framework powders collected from the synthesis of metal-organic framework–nanofiber kebabs was also measured (Table 4) and the values were consistent with previous reports for all three of the metal-organic frameworks (Katz MJ et al. *Chem. Commun.* **2013**, 49, 9449).

Table 4. Material properties and catalytic performance towards chemical warfare agent simulant degradation.

	BET Surface Area (m ² /g)	MOF wt%	DMNP <i>t</i> _{1/2} (min)	Ref.
UiO-66	1512	100	22	This work
	1580 ^a	100	24, 45	Katz MJ et al. <i>Angew. Chem. Int. Ed Engl.</i> 2014 , 53, 497; Peterson GW et al. <i>Inorg. Chem.</i> 2015 , 54, 9684
UiO-66-NH ₂	1334	100	2.8	This work
	1200 ^a	100	0.7	Peterson GW et al. <i>Inorg. Chem.</i> 2015 , 54, 9684
UiO-67	2250	100	7.7	This work
	2500 ^a	100	3.8	Peterson GW et al. <i>Inorg. Chem.</i> 2015 , 54, 9684
PA-6@TiO ₂ @UiO-66	143.9	8.8	135	This work
PA-6@TiO ₂ @UiO-66-NH ₂	205.9	14.7	7.3	This work
PA-6@TiO ₂ @UiO-67	356.2	15.4	7.4	This work
PA-6@TiO ₂	11.5	0	1170	This work
PA-6	11.5	0	3950	This work

^a BET surface area values are adapted from Katz MJ et al. *Chem. Commun.* **2013**, 49, 9449.

5 It is difficult to analyze the metal-organic framework mass fraction in the composites directly by weighing methods. The net mass increase due to metal-organic framework loading is at mg scale and often comparable to the expected mass change due to water uptake by the hygroscopic nylon nanofibers. Using the BET surface area of the metal-organic framework–nanofiber kebab composites and the corresponding bulk metal-organic framework powders, the

10 metal-organic framework mass fraction in the metal-organic framework–nanofiber kebab structures could be estimated (calculation details described above). The calculated metal-organic framework mass fraction is 8.8 %, 14.7 %, and 15.4 % for PA-6@TiO₂@UiO-66, PA-6@TiO₂@UiO-66-NH₂, and PA-6@TiO₂@UiO-67, respectively. These results were further confirmed by elemental analysis using inductively coupled plasma optical emission spectroscopy

15 (ICP-OES; Table 5).

Table 5. Metal-organic framework mass fraction in metal-organic framework-nanofiber composites calculated from BET results and ICP-OES analysis

	Overall BET Surface Area (m ² /g)	MOF Surface Area (m ² /g)	Substrate Surface Area (m ² /g)	MOF wt% Calculated from BET Results (%)	Measured Zr wt% in composite (%)	Measured Zr wt% in MOF (%)	MOF wt% Calculated from ICP Results (%)
PA-6@TiO ₂ @UiO-66	143.9	1512	11.5	8.82	2.81	33.0	8.51
PA-6@TiO ₂ @UiO-66-NH ₂	205.9	1334	11.5	14.7	4.80	29.7	16.2
PA-6@TiO ₂ @UiO-67	356.2	2250	11.5	15.4	4.51	27.2	16.6

The mechanism for forming these metal-organic framework–nanofiber kebab structures was also investigated. Using a similar solvothermal recipe and procedure, UiO-66-NH₂ thin-films were synthesized on Si wafers. Cross-sectional TEM images, high-resolution EDX mapping (Figure 66a-Figure 66i), and time-of-flight secondary ion mass spectroscopy (TOF-SIMS; Figure 67a-Figure 67e) all confirmed that the ALD TiO₂ layer remains in between the metal-organic framework thin-film and the Si substrate. The unchanged thickness of the TiO₂ layer also indicates no etching of TiO₂ during the solvothermal reaction. Therefore, heterogeneous nucleation followed with rapid crystal growth and film coalescence is likely to be the mechanism for forming such kebab nanostructures (Figure 68).

To evaluate the catalytic property of the metal-organic framework–nanofiber kebab composites for chemical warfare agent destruction, the hydrolysis of simulant 4-nitrophenyl phosphate (DMNP; Figure 69a) was analyzed. Specifically, 2.5 mg of metal-organic framework powders or 14 mg of metal-organic framework–nanofiber kebabs catalyst was dispersed in an aqueous buffer solution of *N*-ethylmorpholine (0.45 M, pH 10), and the degradation kinetics of DMNP were characterized using a procedure similar to previous reports (Katz MJ et al. *Angew. Chem. Int. Ed.* **2014**, *53*, 49; Mondloch JE et al. *Nat. Mater.* **2015**, *14*, 512). The reaction progress was monitored by tracking the increased absorbance at 407 nm, which corresponds to *p*-nitrophenoxide (Figure 69b), and calculated the concentration based on the Lambert–Beer Law. The percent conversion of DMNP is plotted as a function of time in Figure 69c– Figure 69e. For metal-organic framework powders, 95%, 98%, and 96% DMNP conversion in 60 min of reaction was observed when UiO-66, UiO-66-NH₂, and UiO-67 were used, respectively. The half-lives (*t*_{1/2}) of DMNP with metal-organic framework powder catalysts (Table 4) showed similar trends

to the reported data. UiO-66-NH₂ exhibits the fastest degradation rate ($t_{1/2} = 2.8$ min) among the three metal-organic framework powders, while UiO-67 also significantly reduces the half-life of DMNP compared to UiO-66. The amine moiety in UiO-66-NH₂ is thought to function as a Brønsted base to enhance the catalytic activity (Katz MJ et al. *Chem. Sci.* **2015**, 6, 2286), while the large pore size of UiO-67 may allow faster diffusion and/or more access of DMNP molecules into the active sites of the metal-organic framework (Peterson GW et al. *Inorg. Chem.* **2015**, 54, 9684; Moon SY et al. *Inorg. Chem.* 2015, 54, 10829).

For untreated PA-6 nanofibers, DMNP shows negligible rate of hydrolysis with an estimated $t_{1/2}$ value over 65 h (Figure 70). With TiO₂ ALD coatings, PA-6@TiO₂ reduces the half-life to ~ 20 h, consistent with the reported reactivity of TiO₂ for chemical warfare agents (Wagner GW et al. *J. Phys. Chem. C* **2008**, 112, 11901; Wagner GW et al. *Ind. Eng. Chem. Res.* **2012**, 51, 3598). Compared with PA-6 and PA-6@TiO₂, metal-organic framework-nanofiber kebab structures exhibit significantly enhanced catalytic performance. Both PA-6@TiO₂@UiO-66-NH₂ and PA-6@TiO₂@UiO-67 enable short half-life of DMNP (7.3 min and 7.4 min, respectively) and high conversion (> 90 %) in 60 min. PA-6@TiO₂@UiO-66 shows a slower DMNP hydrolysis rate, owing to the smaller metal-organic framework mass-loading in the composite structure and the lower catalytic activity of UiO-66. Detailed analyses of the reaction kinetics are shown in Figure 71a-Figure 71f, Figure 72a-Figure 72f, and Table 6. The extent of reaction stops immediately once the metal-organic framework-nanofiber catalyst is removed from the solution (Figure 73), indicating this catalytic reaction is heterogeneous.

Table 6. Kinetic constants and half-lives of DMNP hydrolysis with UiO metal-organic framework powders and UiO metal-organic framework thin films on PA-6@TiO₂ nanofibers.

	k (min ⁻¹)	Calculated $t_{1/2}$ (min)	Observed $t_{1/2}$ (min)	MOF wt%	TOF (s ⁻¹)
UiO-66	0.046	15	22	100	0.0054
UiO-66-NH ₂	0.23	3.0	2.8	100	0.045
UiO-67	0.076	9.1	7.7	100	0.020
PA-6@TiO ₂ @UiO-66	0.0061	113	135	8.8	0.0018
PA-6@TiO ₂ @UiO-66-NH ₂	0.078	8.9	7.3	14.7	0.021
PA-6@TiO ₂ @UiO-67	0.097	7.1	7.4	15.4	0.024

*The amounts of catalysts used in DMNP degradation are 2.5 mg for UiO metal-organic framework powders and 14 mg for metal-organic framework-nanofiber composites. Turnover frequency (TOF) was calculated at $t_{1/2}$, although initial reaction rates give slightly higher TOF values.

SEM images and EDX spectra taken for the metal-organic framework–nanofiber kebabs after DMNP degradation (Figure 74 a-Figure 74f) show that significant amounts of Zr-based metal-organic framework coatings remain in the composites even after strong agitation during the experiments. XRD and BET data confirm these metal-organic framework coatings are still crystalline and porous (Figure 75a-Figure 75b). These results all demonstrate the good adhesion of the metal-organic framework thin-films to the nanofiber substrates. Although these metal-organic framework-coated nanofibers were not designed for recyclable protection from chemical warfare agents due to potential secondary contamination during regeneration, the metal-organic framework–nanofiber kebab catalysts still show high reactivity during the 2nd cycle of DMNP testing, and noticeable catalytic effect in the 3rd cycle (Figure 76).

In addition to simulant DMNP, the metal-organic framework–nanofiber kebab composites were tested for the destruction of nerve agent GD (Figure 77a). For this test, 2.6 mL of GD was added to approximately 14 mg of metal-organic framework–nanofiber catalyst in an NMR tube, followed with vigorous shaking. GD concentration was determined using ³¹P NMR (Figure 77b). The doublet peaks at approximately 40 and 33 ppm associated with GD immediately decreased upon exposure to the metal-organic framework–nanofibers (Figure 78–Figure 80). The pinacolyl methylphosphonic acid (PMPA) peak (approximately 27 ppm) began growing at the same time, indicating detoxification of the chemical warfare agent to a non-toxic product. The half-lives of GD were 3.0 min with PA-6@TiO₂@UiO-66, 3.7 min with PA-6@TiO₂@UiO-66-NH₂, and 2.3 min with PA-6@TiO₂@UiO-67. All three of the metal-organic framework–nanofiber composites showed fast GD destruction (*t*_{1/2}, 4 min) and high conversion (+ 80 %) within 10 min. The fastest reaction rate with PA-6@TiO₂@UiO-67 is possibly because the large pore size of UiO-67 allows diffusion of reactants into the pores while the catalytic reactions occur mainly on the external surface of UiO-66 and UiO-66-NH₂ (Peterson GW et al. *Inorg. Chem.* **2015**, *54*, 9684). These results indicate that conformal metal-organic framework thin-films grown onto nanofiber substrates can achieve excellent catalytic activity even with small metal-organic framework loadings (< 20 %). This advantage can benefit the end users by providing substantial catalytic efficacy at a reduced burden.

In conclusion, a series of metal-organic framework–nanofiber kebab structures capable of decomposing the chemical warfare agent simulant DMNP and nerve agent GD has been discussed. ALD TiO₂ nucleation layers enhance the heterogeneous nucleation of UiO-type metal-organic framework crystals and enable the formation of kebab structures with strong attachment to the substrates. Using these metal-organic framework–nanofiber composites, the half-lives of

DMNP and GD are as short as 7.3 min and 2.3 min, respectively, indicating great promise of the metal-organic framework–nanofibers for chemical warfare agent protection. The synthesis method and the metal-organic framework–nanofiber composite structures presented herein offer new opportunities to advance the development of gas filters, chemical sensors, and potentially smart textile materials to protect against harmful air pollutants.

Other advantages which are obvious and which are inherent to the invention will be evident to one skilled in the art. It will be understood that certain features and sub-combinations are of utility and may be employed without reference to other features and sub-combinations.

This is contemplated by and is within the scope of the claims. Since many possible embodiments may be made of the invention without departing from the scope thereof, it is to be understood that all matter herein set forth or shown in the accompanying drawings is to be interpreted as illustrative and not in a limiting sense.

The methods of the appended claims are not limited in scope by the specific methods described herein, which are intended as illustrations of a few aspects of the claims and any methods that are functionally equivalent are intended to fall within the scope of the claims. Various modifications of the methods in addition to those shown and described herein are intended to fall within the scope of the appended claims. Further, while only certain representative method steps disclosed herein are specifically described, other combinations of the method steps also are intended to fall within the scope of the appended claims, even if not specifically recited. Thus, a combination of steps, elements, components, or constituents may be explicitly mentioned herein or less, however, other combinations of steps, elements, components, and constituents are included, even though not explicitly stated.

CLAIMS

What is claimed is:

1. A method of making a metal-organic framework, the method comprising:
contacting a metal oxide with a metal salt to form a hydroxy double salt; and
contacting the hydroxy double salt with an organic linker to form the metal-organic framework.
2. The method of claim 1, wherein the metal oxide and the metal salt are provided in a molar ratio of from 1:100 to 1:1.
3. The method of claim 2, wherein the metal oxide and the metal salt are provided in a molar ratio of from 1:50 to 1:1.
4. The method of claim 2 or claim 3, wherein the metal oxide and the metal salt are provided in a molar ratio of from 1:20 to 1:1.
5. The method of any one of claims 2-4, wherein the metal oxide and the metal salt are provided in a molar ratio of from 1:10 to 1:1.
6. The method of any one of claims 2-5, wherein the metal oxide and the metal salt are provided in a molar ratio of from 1:5 to 4:5.
7. The method of any one of claims 1-6, wherein the metal oxide is contacted with the metal salt and the organic linker substantially simultaneously to form the hydroxy double salt *in situ*.
8. The method of any one of claims 1-7, wherein the metal oxide comprises a powder, the powder comprising a plurality of particles having an average particle size of from 5 nm to 10,000 nm.
9. The method of claim 8, wherein the plurality of particles have an average particle size of from 5 nm to 1,000 nm.
10. The method of claim 8 or claim 9, wherein the plurality of particles have an average particle size of from 5 nm to 500 nm.

11. The method of any one of claims 8-10, wherein the plurality of particles have an average particle size of from 200 nm to 300 nm.
12. The method of any one of claims 1-11, further comprising forming a slurry of the metal oxide powder by dispersing the metal oxide powder in a solvent.
13. The method of any one of claims 1-7, wherein the metal oxide comprises a film having a thickness of from 1 nm to 10,000 nm.
14. The method of claim 13, wherein the metal oxide film has a thickness of from 1 nm to 1,000 nm.
15. The method of claim 13 or claim 14, wherein the metal oxide film has a thickness of from 1 nm to 500 nm.
16. The method of any one of claims 13-15, wherein the metal oxide film has a thickness of from 1 nm to 100 nm.
17. The method of any one of claims 13-16, wherein the metal oxide film has a thickness of from 30 nm to 40 nm.
18. The method of any one of claims 13-17, further comprising depositing the film of the metal oxide onto a substrate.
19. The method of claim 18, wherein depositing the metal oxide film comprises atomic layer deposition, chemical vapor deposition, electron beam evaporation, thermal evaporation, sputtering deposition, pulsed laser deposition, or combinations thereof.
20. The method of any one of claims 13-19, further comprising patterning the metal oxide film before the hydroxy double salt is formed.
21. The method of claim 20, wherein patterning the metal oxide film comprises:
 - depositing a radiation sensitive material on the layer of the metal oxide deposited on the substrate;
 - exposing a portion of the radiation sensitive material to radiation; and

developing the exposed radiation sensitive material to remove at least a portion of the radiation sensitive material, thereby patterning the radiation sensitive material on the metal oxide film.

22. The method of claim 21, wherein the portion of radiation sensitive material removed comprises the portion of the radiation sensitive material that was exposed to radiation.
23. The method of claim 21 or claim 22, further comprising removing the remainder of the radiation sensitive material after the patterned metal oxide film has been contacted with the metal salt to form a patterned hydroxy double salt, or after the patterned hydroxy double salt has been contacted with the organic linker to form a patterned metal-organic framework.
24. The method of any one of claims 22-23, wherein the radiation sensitive material comprises a photoresist, an electron-sensitive resist, or a combination thereof.
25. The method of any one of claims 21-24, wherein the radiation comprises electromagnetic radiation, electron beam radiation, ion beam irradiation, or a combination thereof.
26. The method of any one of claims 8-12, further comprising depositing the metal oxide powder onto a substrate.
27. The method of claim 26, wherein depositing the metal oxide powder comprises printing, lithographic deposition, spin coating, drop-casting, zone casting, dip coating, blade coating, spraying, vacuum filtration, slot die coating, curtain coating, or combinations thereof.
28. The method of any one of claims 18-27, wherein the substrate comprises a plurality of polymer particles, a polymer film, a semiconductor wafer, a plurality of polymer fibers, or a combination thereof.
29. The method of claim 28, wherein the substrate comprises a plurality of polystyrene spheres, a silicon wafer, a plurality of polypropylene fibers, a plurality of polyacrylonitrile fibers, a plurality of polyamide fibers, or a combination thereof.

30. The method of any one of claims 1-29, wherein the metal oxide comprises a metal selected from the group consisting of Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Pd, Sn, Sr, Ti, V, Zn, and combinations thereof.
31. The method of any one of claims 1-30, wherein the metal oxide comprises ZnO, TiO₂, or a combination thereof.
32. The method of any one of claims 1-31, wherein the metal salt comprises a metal selected from the group consisting of Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Pd, Sn, Sr, V, Zn, Zr, and combinations thereof.
33. The method of claim 32, wherein the metal salt comprises Cu(NO₃)₂, Zn(OAc)₂, ZrCl₄, or a combination thereof.
34. The method of any one of claims 1-33, wherein the metal oxide comprises a first metal; the metal salt comprises a second metal; and the first metal is different than the second metal.
35. The method of any one of claims 1-34, wherein the metal-organic framework is formed in an amount of time of from 15 seconds to 24 hours.
36. The method of claim 35, wherein the metal-organic framework is formed in an amount of time of from 15 seconds to 12 hours.
37. The method of claim 35 or claim 36, wherein the metal-organic framework is formed in an amount of time of from 15 seconds to 6 hours.
38. The method of any one of claims 35-37, wherein the metal-organic framework is formed in an amount of time of from 30 seconds to 30 minutes.
39. The method of any one of claims 35-38, wherein the metal organic framework is formed in an amount of time of from 1 minute to 10 minutes.
40. The method of any one of claims 1-39, wherein the organic linker comprises trimesic acid, biphenyldicarboxylic acid, terephthalic acid, 2-methylimidazole, derivatives thereof, or a combination thereof.

41. The method of claim 40, wherein the organic linker comprises biphenyldicarboxylic acid, terephthalic acid or a derivative thereof.
42. The method of claim 41, wherein the derivative of terephthalic acid comprises 2-aminoterephthalic acid, 2-chloroterephthalic acid, 2-nitroterephthalic acid, 2,5-diaminoterephthalic acid, or a combination thereof.
43. The method of any one of claims 1-42, wherein the metal-organic framework is formed at room temperature.
44. The method of any one of claims 1-43, wherein the metal-organic framework comprises a plurality of particles having an average particle size of from 10 nm to 10 μm .
45. The method of claim 44, wherein the metal-organic framework comprises a plurality of particles having an average particle size of from 10 nm to 500 μm .
46. The method of claim 44 or claim 45, wherein the metal-organic framework comprises a plurality of particles having an average particle size of from 100 nm to 50 μm .
47. The method of any one of claims 44-46, wherein the average particle size is from 400 nm to 3 μm .
48. The method of any one of claims 1-47, wherein the metal-organic framework has an adsorption capacity for N_2 gas of from 10 cm^3 of N_2 gas per g of metal-organic framework to 600 cm^3 of N_2 gas per gram of metal-organic.
49. The method of any one of claims 1-48, wherein the metal-organic framework has an adsorption capacity for NH_3 gas of from 3 moles of NH_3 gas per kg of metal-organic framework to 8 moles of NH_3 gas per kg of metal-organic framework.
50. The method of claim 49, wherein the metal-organic framework has an adsorption capacity for NH_3 gas of 4 moles of NH_3 gas or more per kg of metal-organic framework.
51. The method of any one of claims 1-50, wherein the metal-organic framework has an adsorption capacity for H_2S gas of from 3 moles H_2S gas per kg of metal-organic framework to 10 moles H_2S gas per kg of metal-organic framework.

52. The method of claim 51, wherein the metal-organic framework has an adsorption capacity for H₂S gas of 4 moles of H₂S gas or more per kg of metal-organic framework.
53. The method of any one of claims 1-52, wherein the method has a space-time-yield for forming the metal-organic framework of from 1,000 to 40,000 kg·m⁻³·d⁻¹.
54. The method of claim 53, wherein the method has a space-time-yield for forming the metal-organic framework of 10,000 kg·m⁻³·d⁻¹ or more.
55. The method of claim 53 or claim 54, wherein the method has a space-time-yield for forming the metal-organic framework of 30,000 kg·m⁻³·d⁻¹ or more.
56. The method of any one of claims 1-55, wherein the metal-organic framework is formed with a yield of 90% or more.
57. The method of claim 56, wherein the metal-organic framework is formed with a yield of 98% or more.
58. The method of any one of claims 1-57, wherein the metal-organic framework has a BET surface area of from 10 m²/g to 3000 m²/g.
59. The method of claim 58, wherein the metal-organic framework has a BET surface area of 200 m²/g or more.
60. The method of claim 58 or claim 59, wherein the metal-organic framework has a BET surface area of 500 m²/g or more.
61. The method of any one of claims 58-60, the metal-organic framework has a BET surface area of 1250 m²/g or more.
62. The method of any one of claims 58-61, wherein the metal-organic framework has a BET surface area of 1750 m²/g or more.
63. The method of any one of claims 1-62, wherein the metal-organic framework has a pore volume of from 0.2 to 1.5 cm³/g.
64. A metal-organic framework comprising copper and 2-aminoterephthalate.

65. The metal-organic framework or claim 64, wherein the crystal structure for of the metal-organic framework comprises copper paddle wheel units are coordinated to the carboxylic groups in the 2-aminoterephthalate organic linker, forming a triclinic crystal structure.
66. The metal-organic framework of claim 64 or claim 65, wherein the metal-organic framework has a BET surface area of from $28 \text{ m}^2/\text{g}$ to $93 \text{ m}^2/\text{g}$.
67. The metal-organic framework of claim 66, wherein the metal-organic framework has a BET surface area of $50 \text{ m}^2/\text{g}$ or more.
68. The metal-organic framework of any one of claims 64-67, wherein the metal-organic framework has a pore volume of from $0.17 \text{ cm}^3/\text{g}$ to $0.86 \text{ cm}^3/\text{g}$.
69. The metal-organic framework of claim 68, wherein the metal-organic framework has a pore volume of $0.5 \text{ cm}^3/\text{g}$ or more.
70. The metal-organic framework of any one of claims 64-69, wherein the metal-organic framework has an adsorption capacity for NH_3 gas of from 2.6 to 8.2 moles of NH_3 gas per kg of metal-organic framework.
71. The metal-organic framework of any one of claims 64-70, wherein the metal-organic framework has an adsorption capacity for Cl_2 gas of from 0.35 to 3.3 moles of Cl_2 gas or more per kg of metal-organic framework.
72. The metal-organic framework of any one of claims 64-71, wherein the metal-organic framework has an adsorption capacity for NO_2 gas of from 1 to 1.4 moles of NO_2 gas or more per kg of metal-organic framework.
73. A method of making the metal-organic framework of any one of claims 64-72, the method comprising the method of any one of claims 1-63, wherein the metal oxide comprises ZnO , the metal salt comprises Cu , and the organic linker comprises 2-aminoterephthalic acid.
74. A method of making the metal-organic framework of any one of claims 64-72, the method comprising contacting a metal salt with an organic linker to form a mixture; and

- heating the mixture at an elevated temperature for an amount of time; wherein the metal salt comprises Cu and the organic linker comprises 2-aminoterephthalic acid.
75. The method of claim 74, wherein the elevated temperature is from 70°C to 120°C.
76. The method of claim 75, wherein the elevated temperature is from 80°C to 90°C.
77. The method of any one of claims 74-76, wherein the amount of time is from 3 hours to 24 hours.
78. The method of any one of claims 74-77, wherein the mixture further comprises a solvent.
79. The method of claim 78, wherein the solvent comprises DMF.
80. The method of any one of claims 73-79, wherein the metal salt comprises $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$.
81. A filter for removing a gas from a gas stream, said filter comprising the metal-organic framework formed by the method of any one of claims 1-63 or the metal-organic framework of any one of claims 64-72.
82. A filter for removing a fluid from a fluid stream, said filter comprising the metal-organic framework formed by the method of any one of claims 1-63 or the metal-organic framework of any one of claims 64-72.
83. The filter of claim 82, wherein the fluid removed from the fluid stream comprises a toxin.
84. The filter of claim 83, wherein the toxin comprises a toxic industrial chemical, a chemical warfare agent, or a combination thereof.
85. The filter of claim 83 or claim 84, wherein the toxin comprises *O*-pinacolylmethylphosphonofluoridate.
86. The filter of any one of claims 83-85, wherein the metal-organic framework degrades the toxin.
87. The filter of claim 86, wherein the toxin has a half-life of 10 minutes or less on the metal-organic framework.

88. The filter of claim 86 or claim 87, wherein the toxin has a half-life of 5 minutes or less on the metal-organic framework.
89. The filter of any one of claims 86-88, wherein the toxin has a half-life of 3 minutes or less on the metal-organic framework.
90. A respirator, said respirator comprising the filter of any one of claims 81-89.
91. A gas mask, said gas mask comprising the filter of any one of claims 81-89.
92. A human protection device, comprising a fabric and the metal-organic framework formed by the method of any one of claims 1-63 or the metal-organic framework of any one of claims 64-72.

1/45

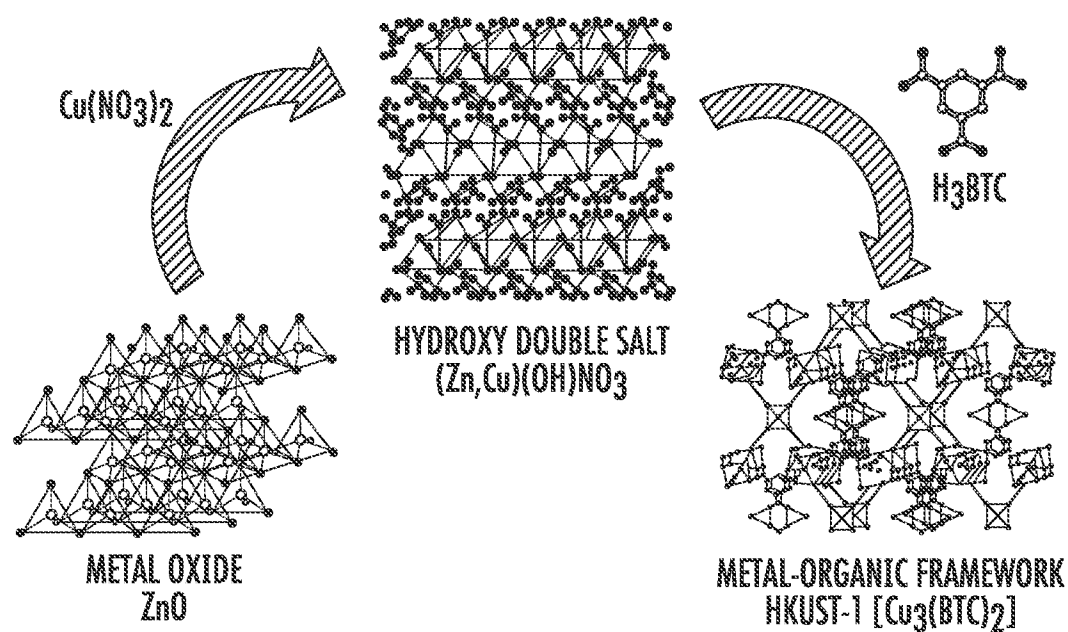


FIG. 1

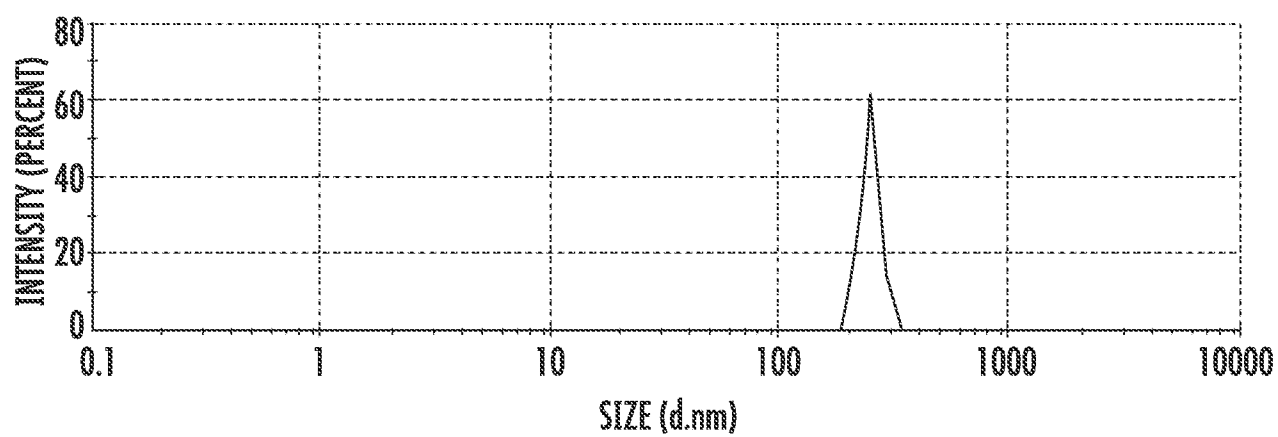


FIG. 2

2/45

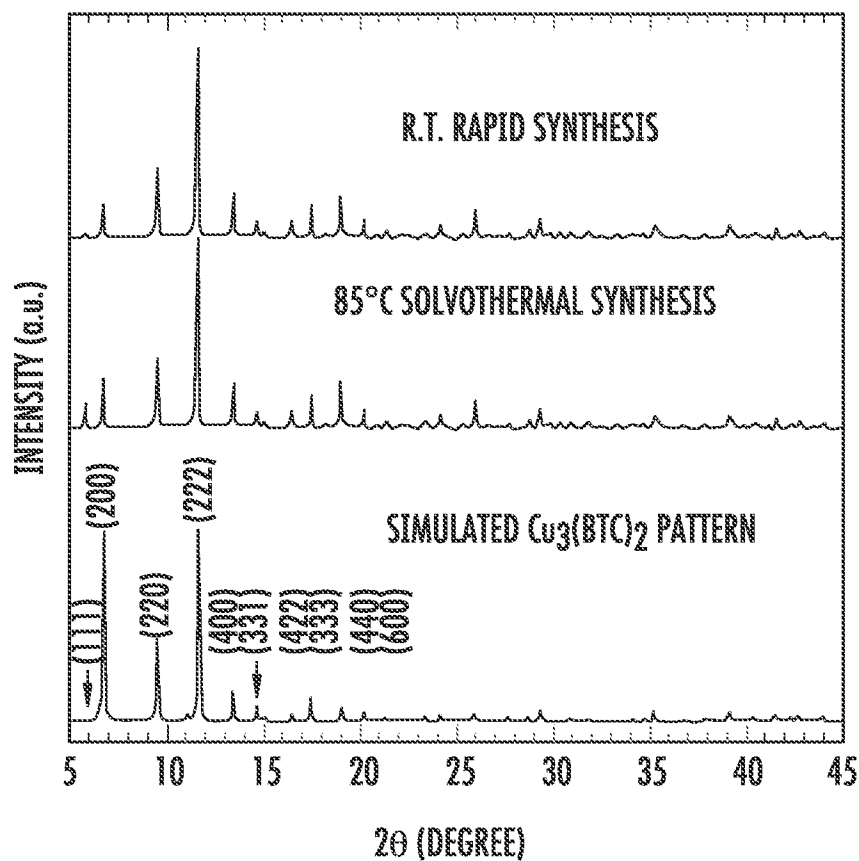


FIG. 3

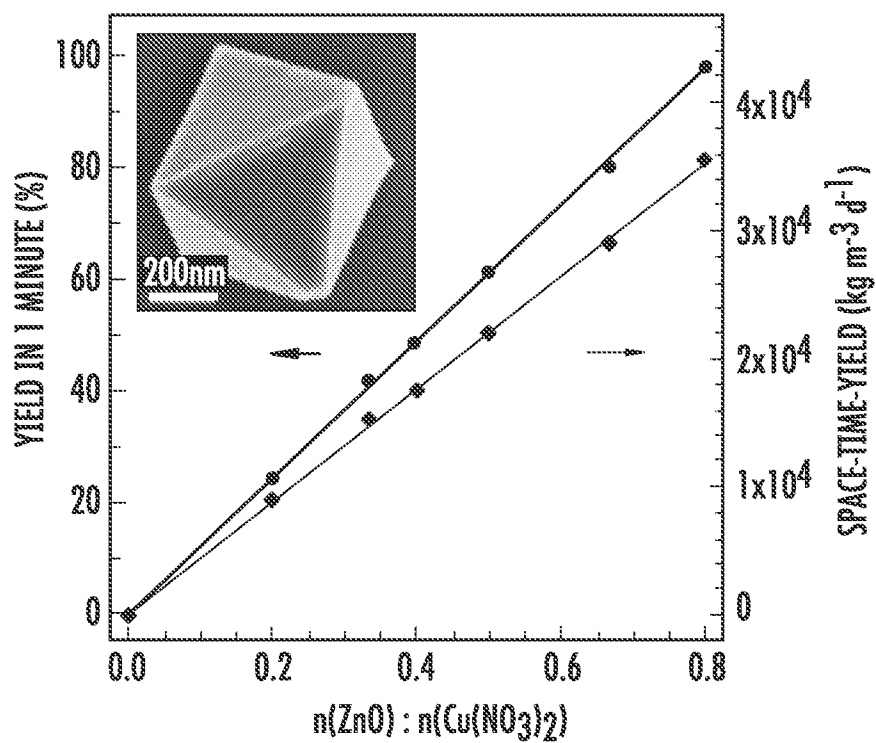


FIG. 4

3/45

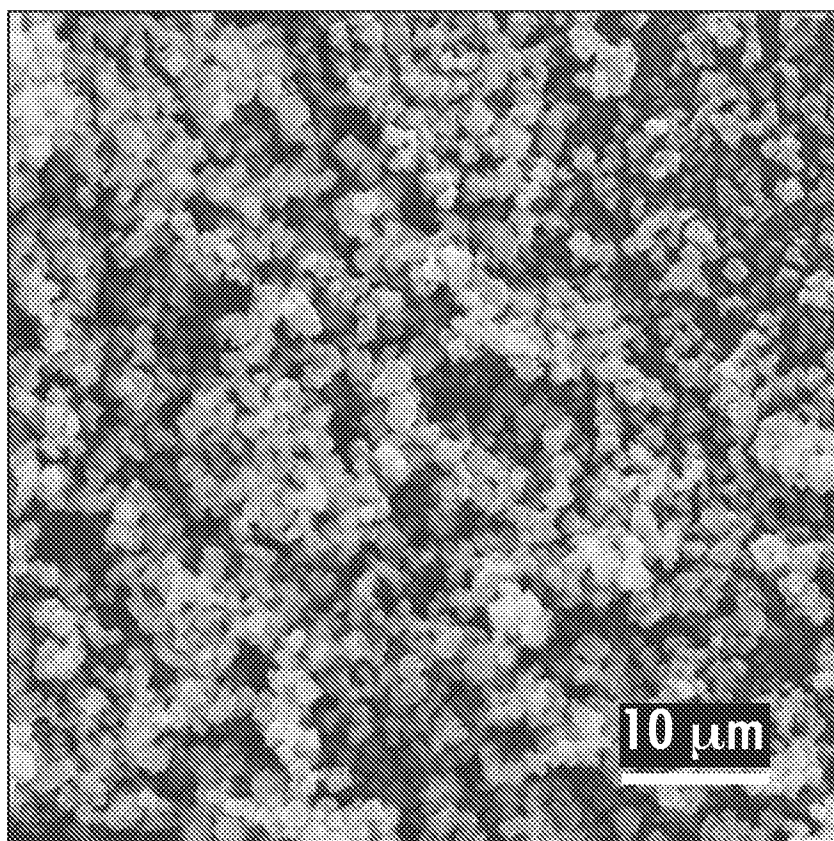


FIG. 5

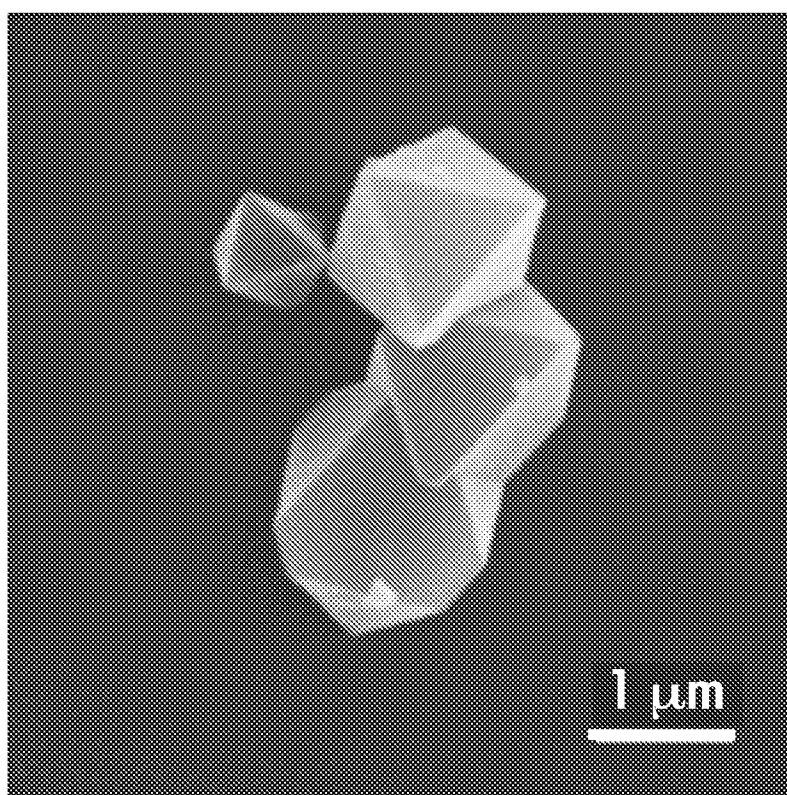


FIG. 6

4/45

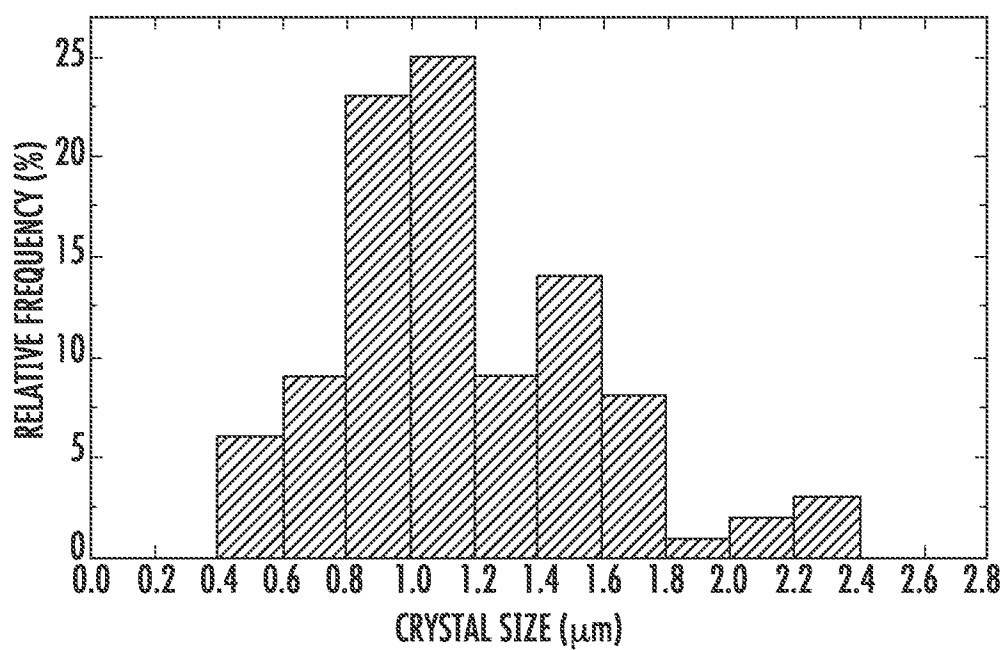


FIG. 7

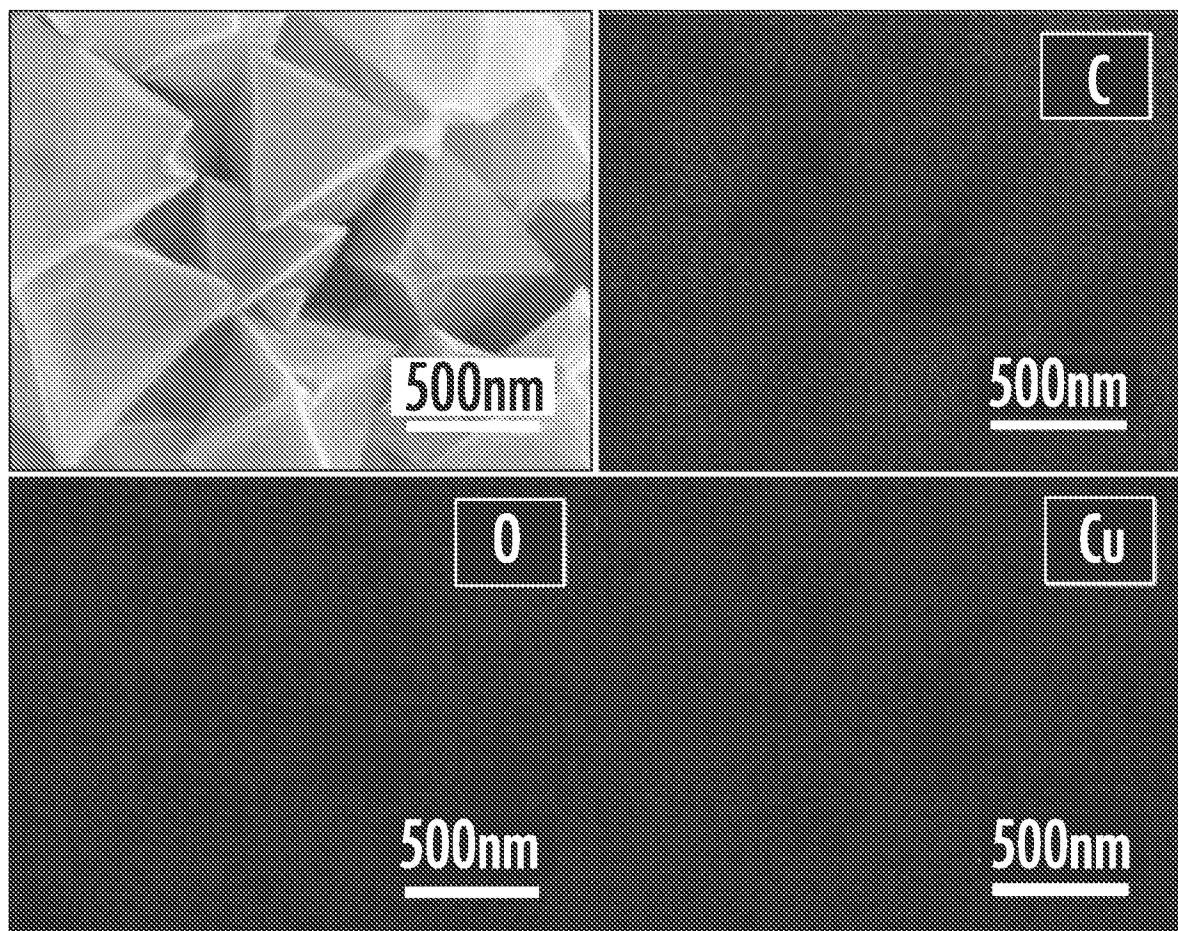


FIG. 8

5/45

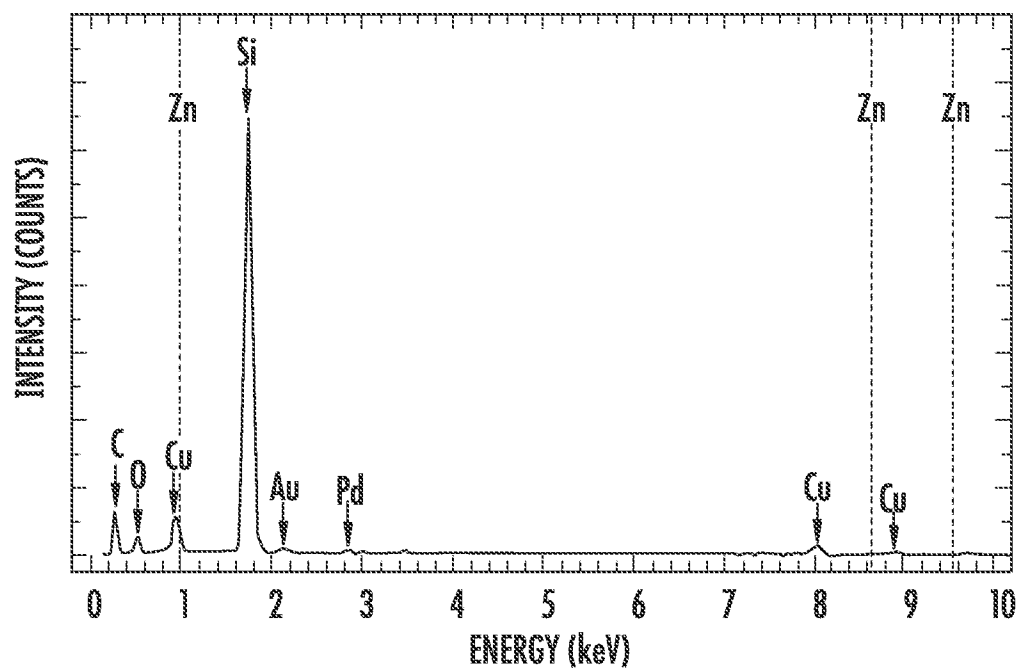


FIG. 9

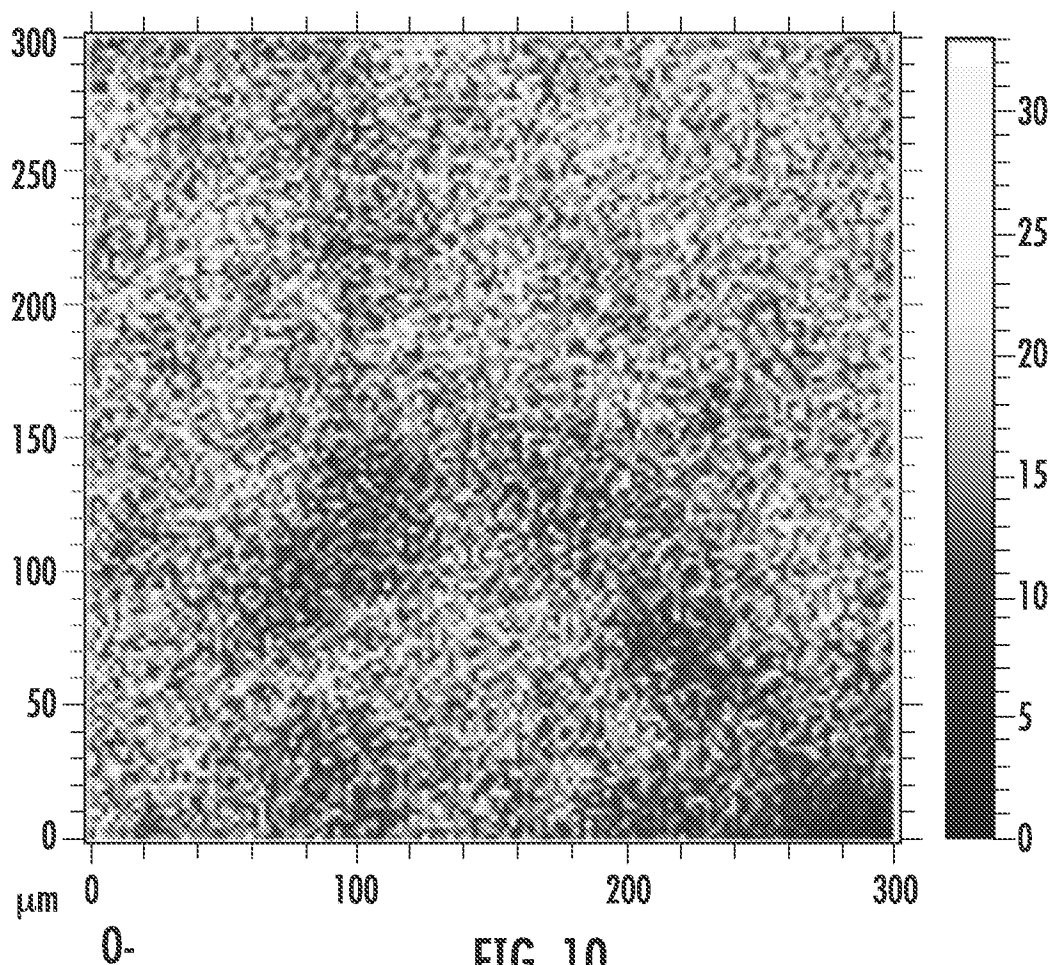
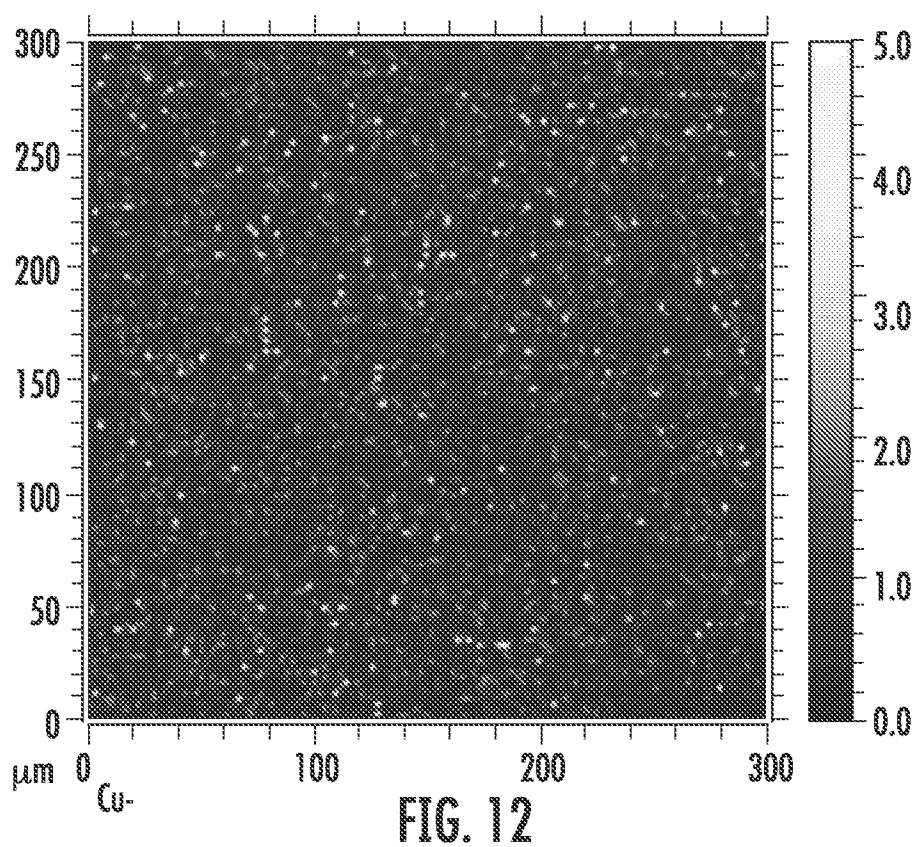
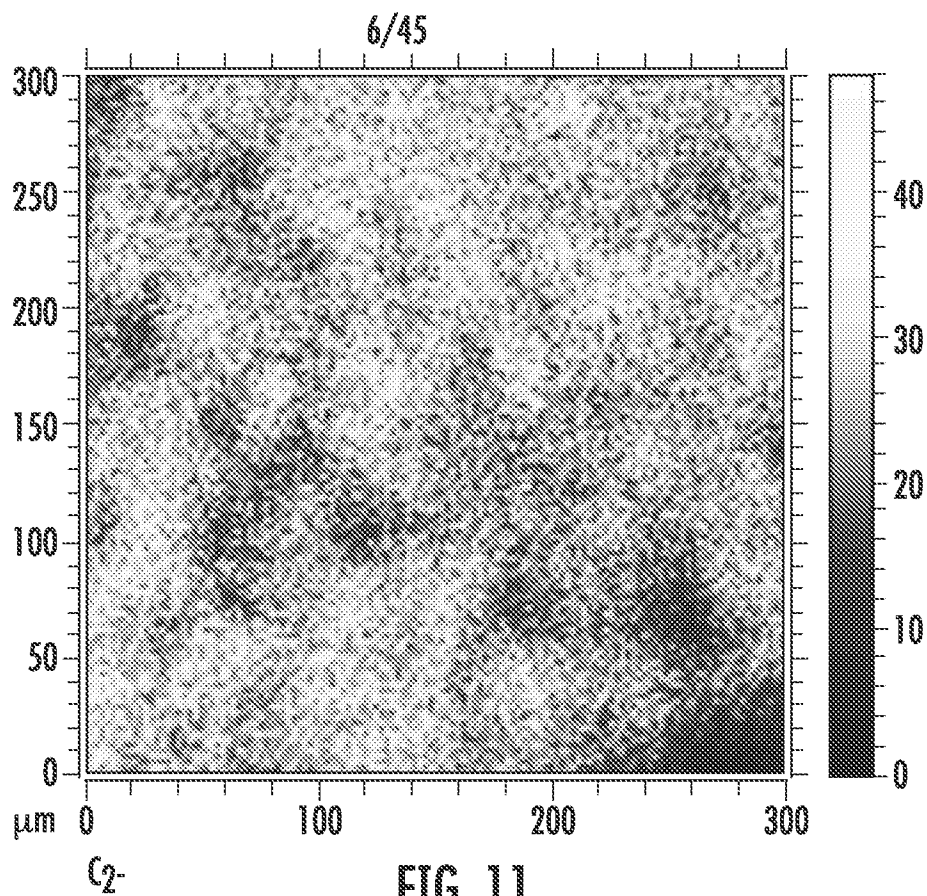


FIG. 10



7/45

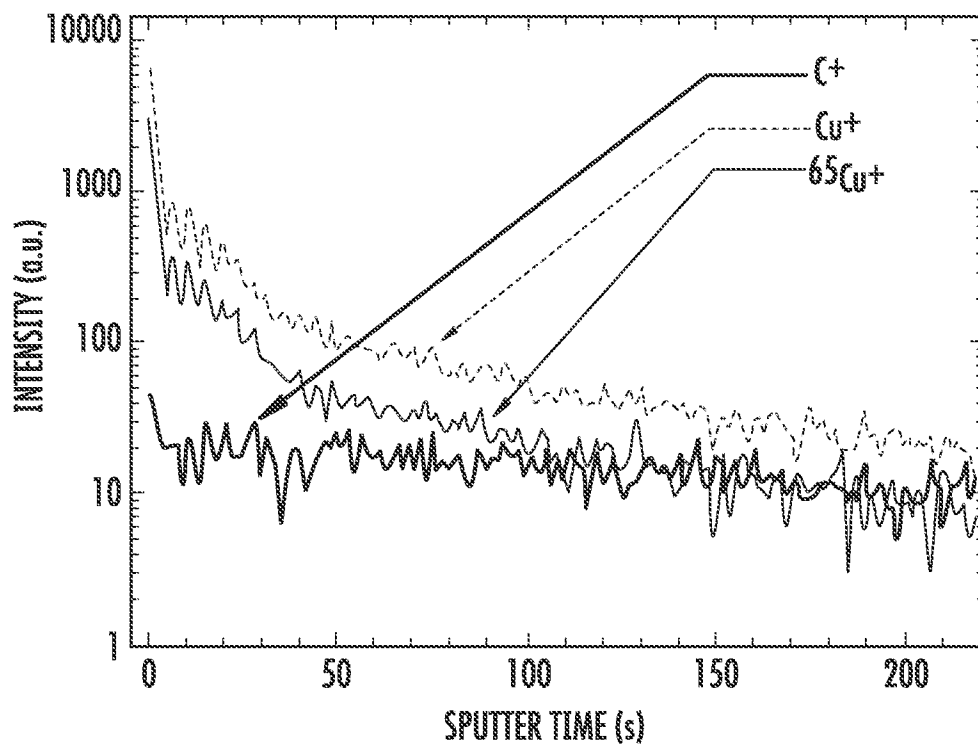


FIG. 13

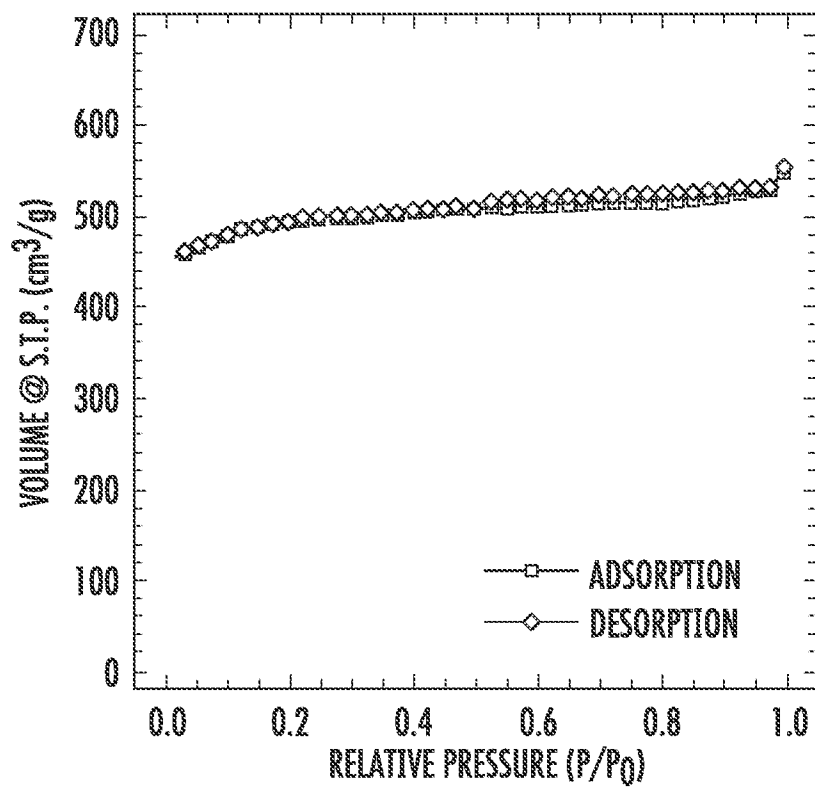


FIG. 14

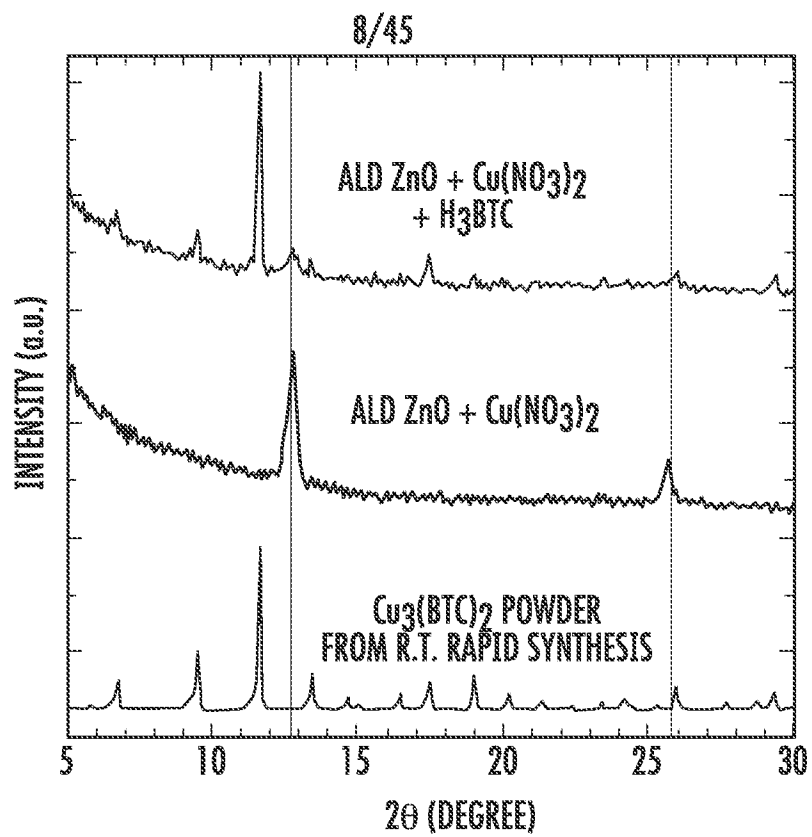


FIG. 15

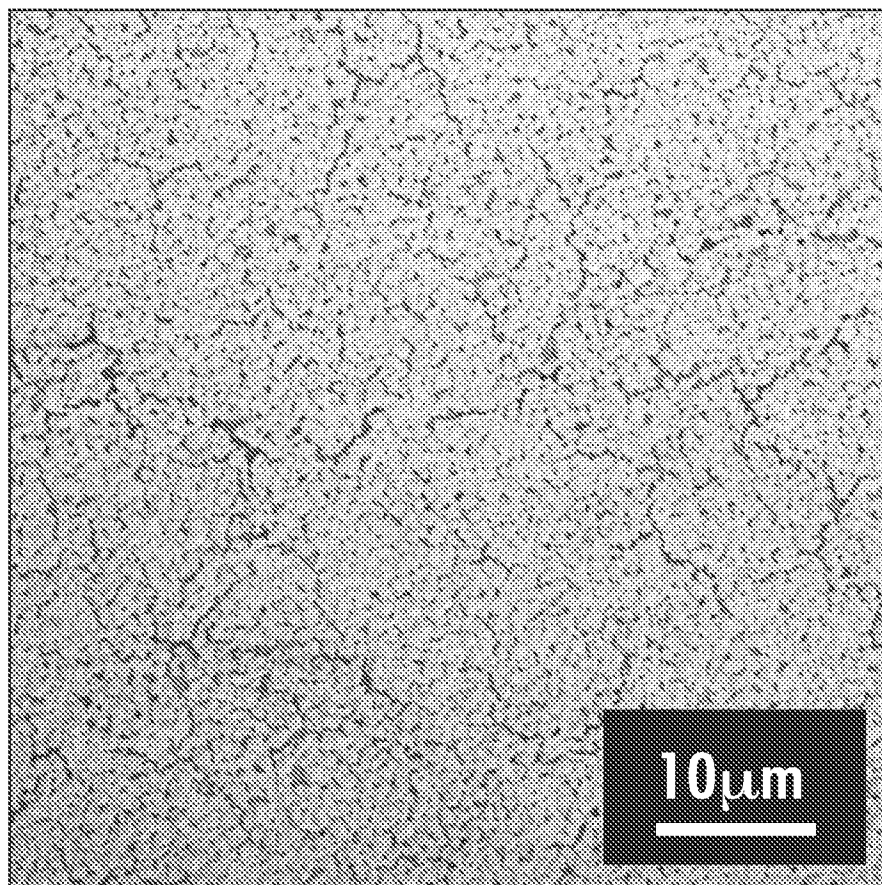


FIG. 16

9/45

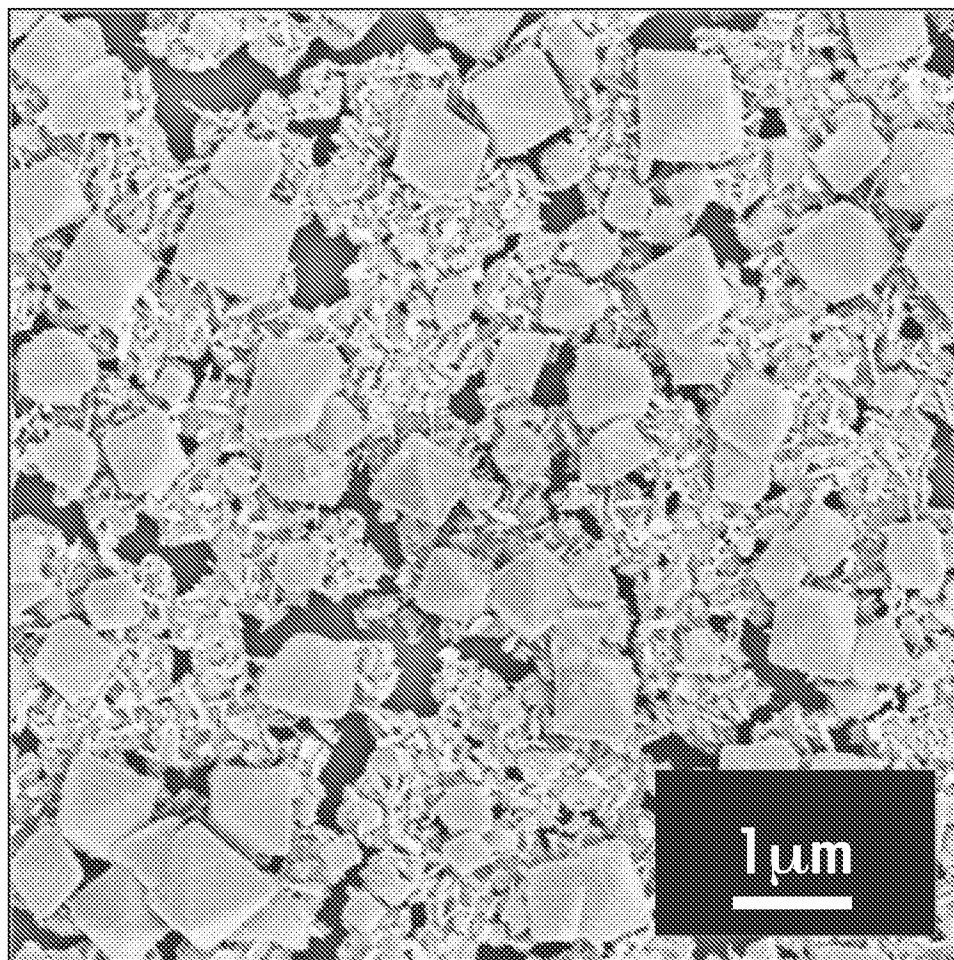


FIG. 17

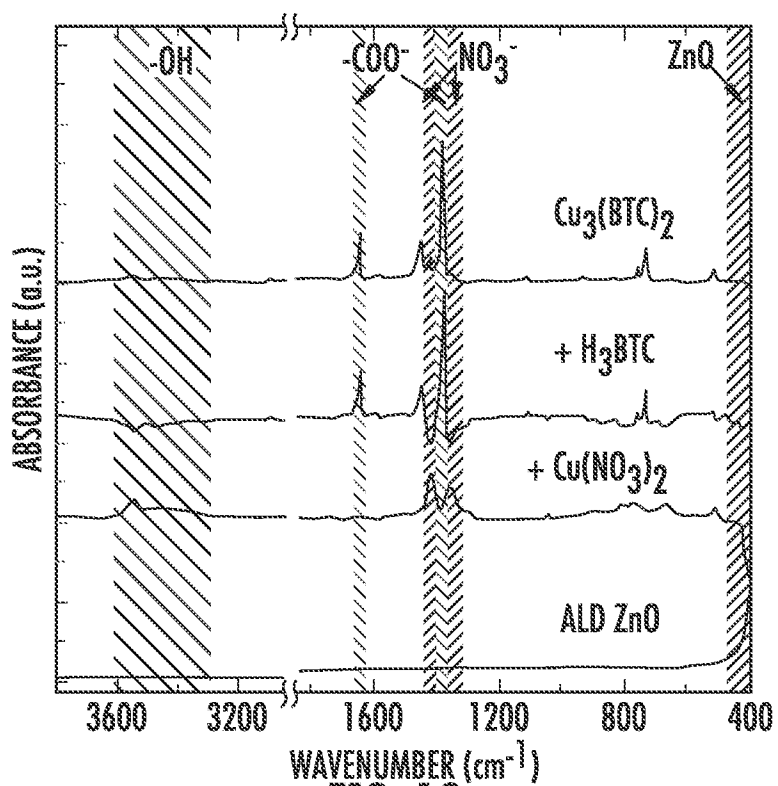


FIG. 18

10/45

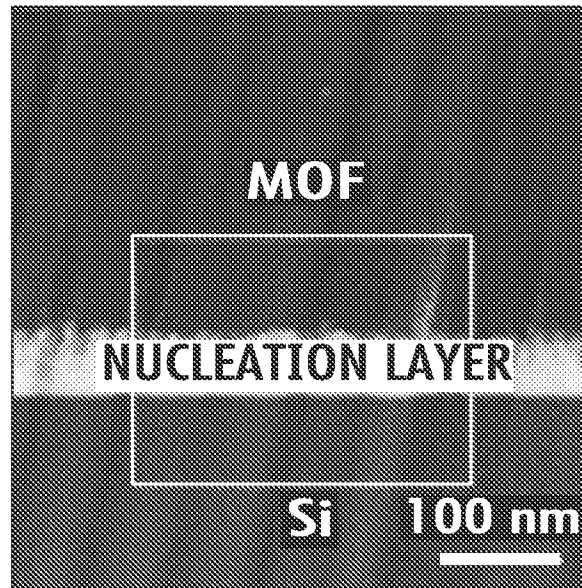


FIG. 19

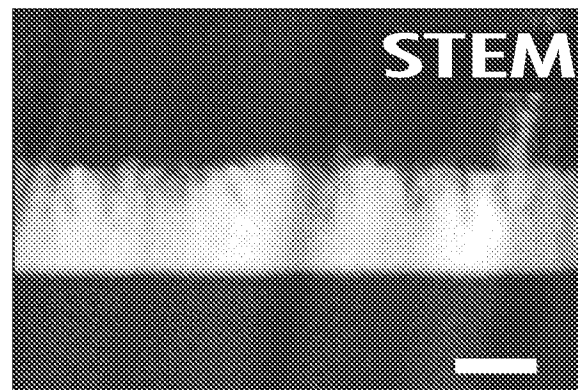


FIG. 20

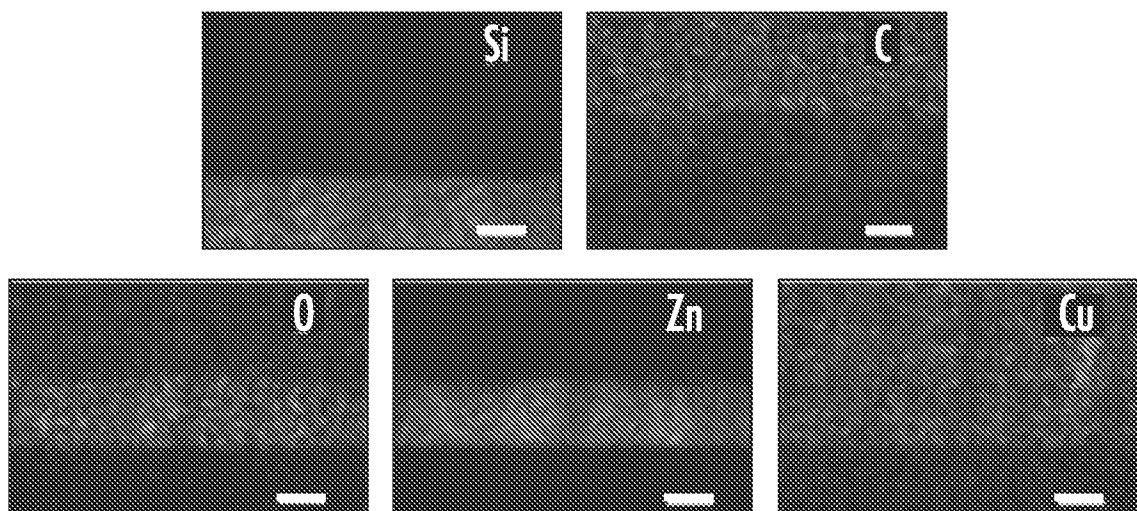


FIG. 21

11/45

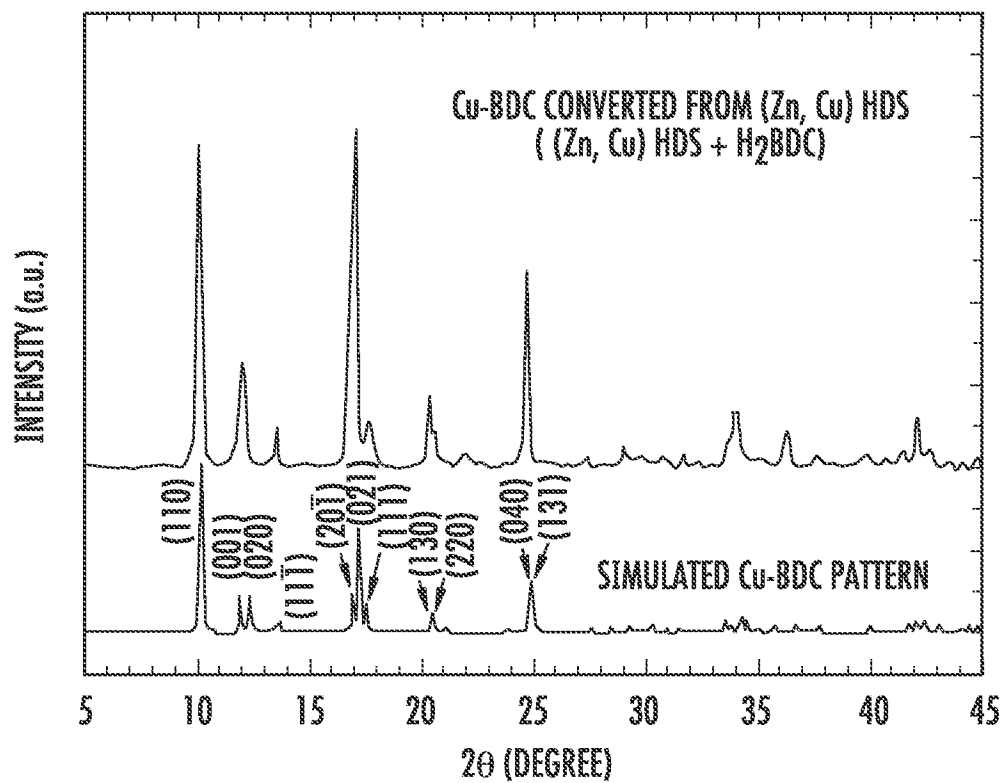


FIG. 22

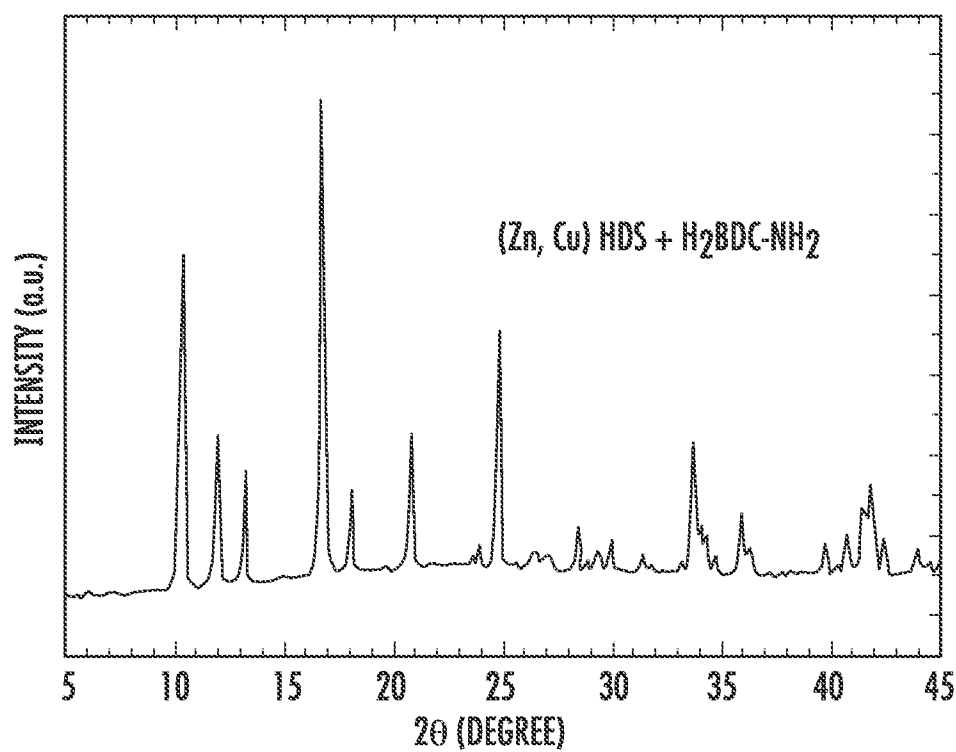


FIG. 23

12/45

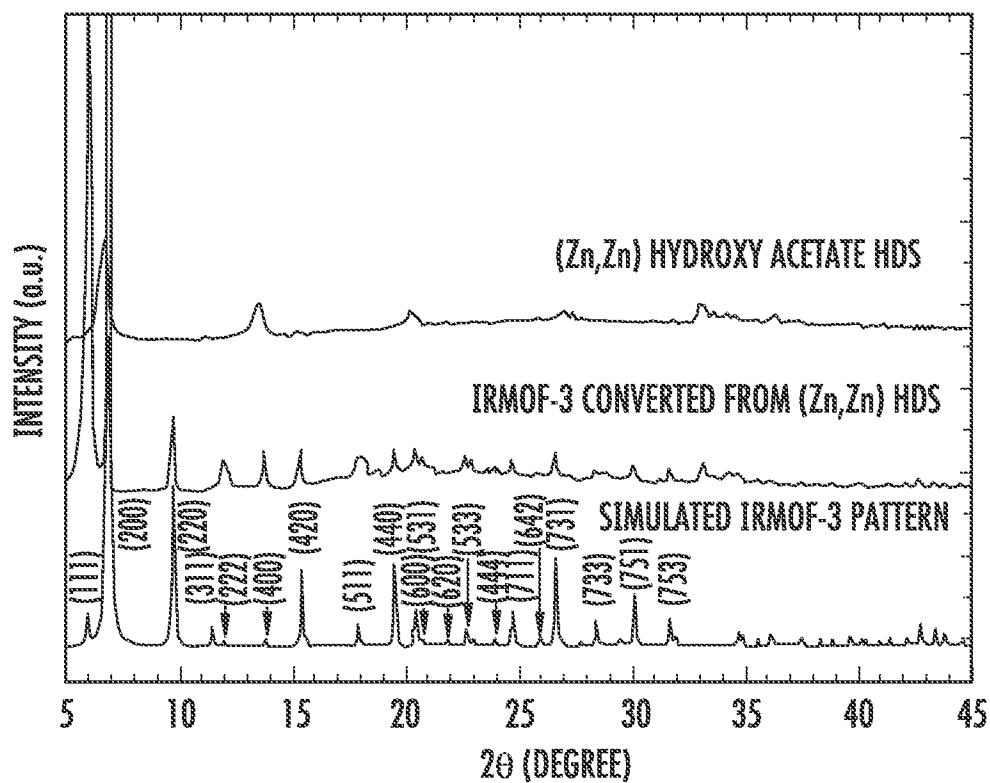


FIG. 24

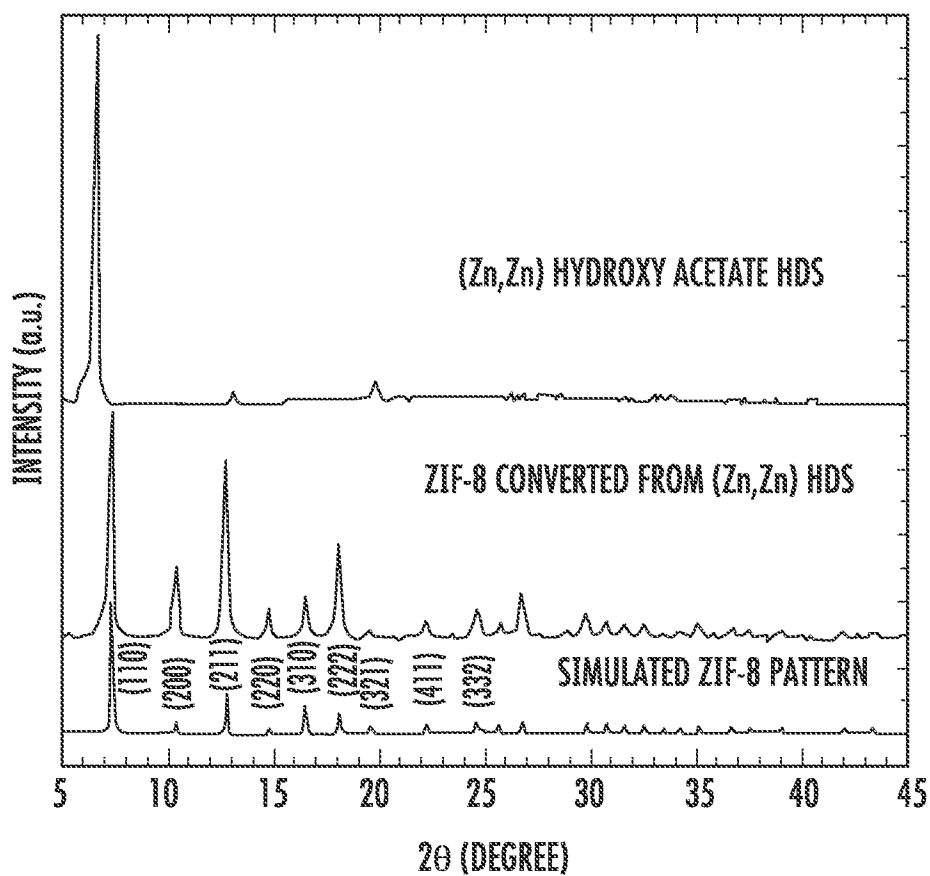


FIG. 25

13/45

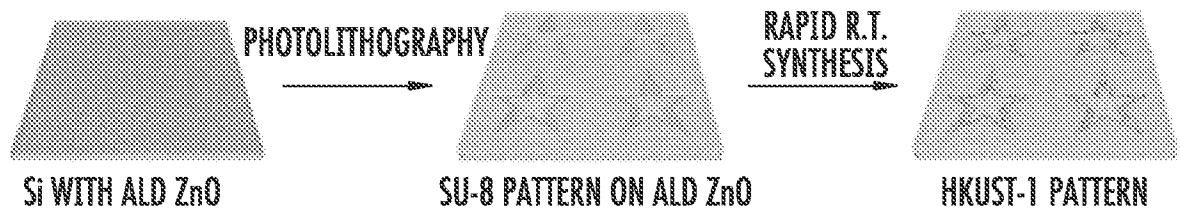


FIG. 26

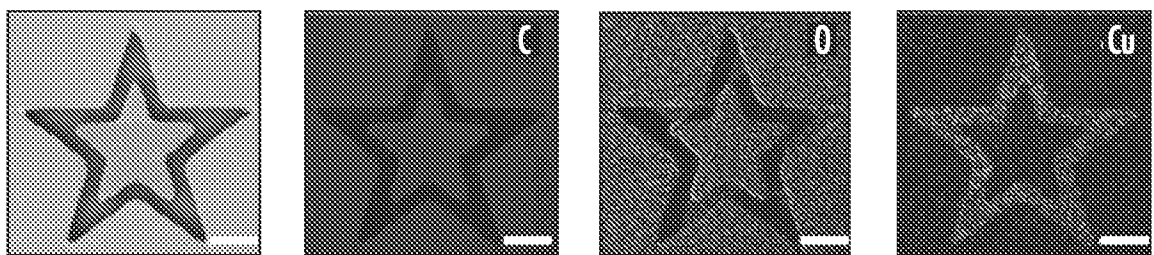


FIG. 27

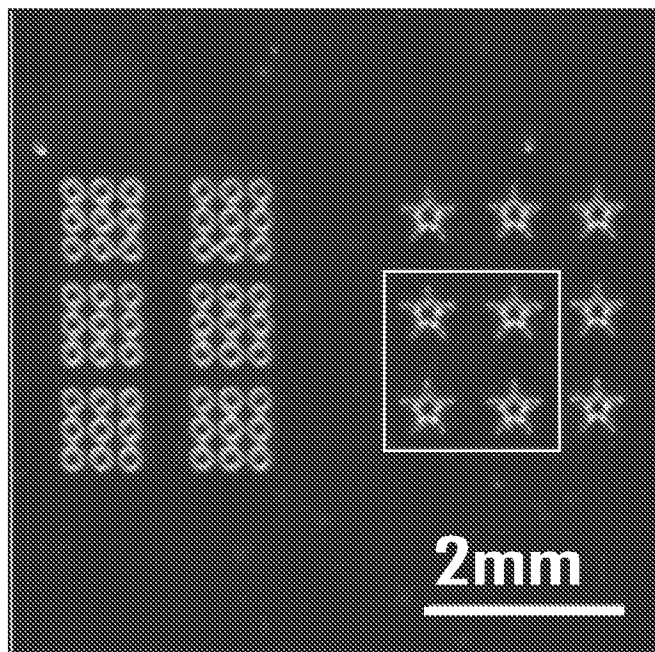


FIG. 28

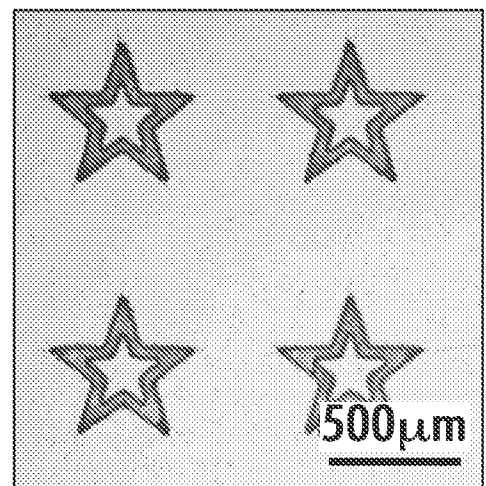


FIG. 29

14/45

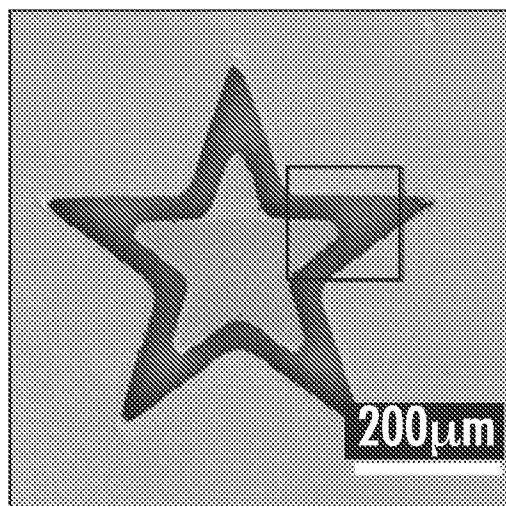


FIG. 30

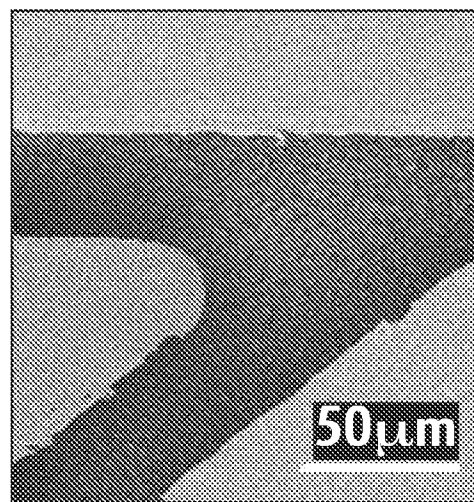


FIG. 31

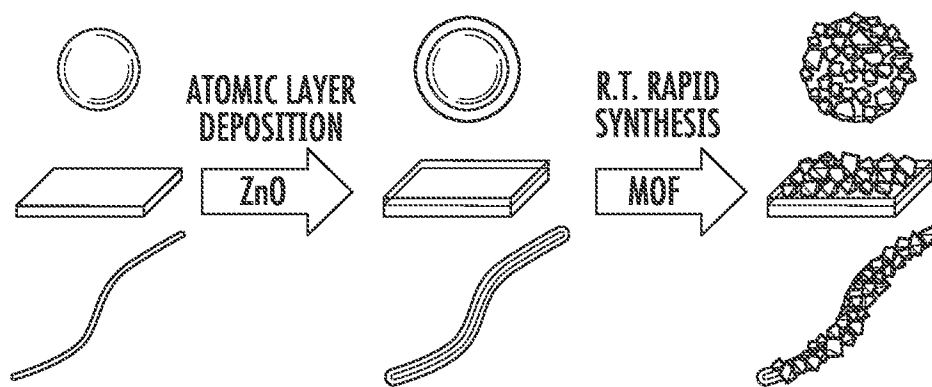


FIG. 32

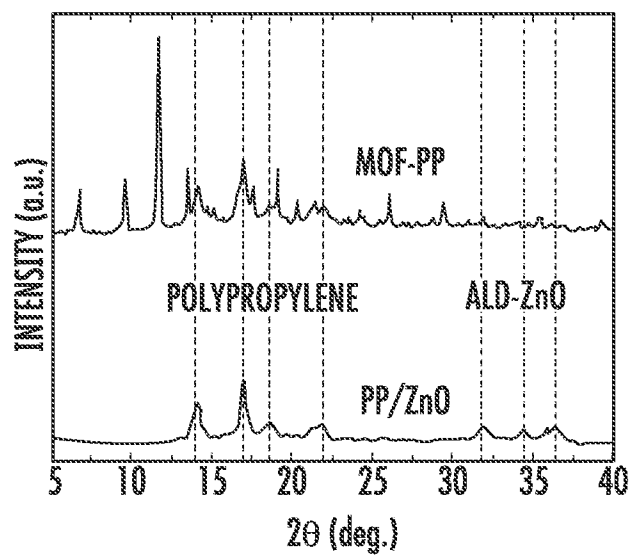


FIG. 33

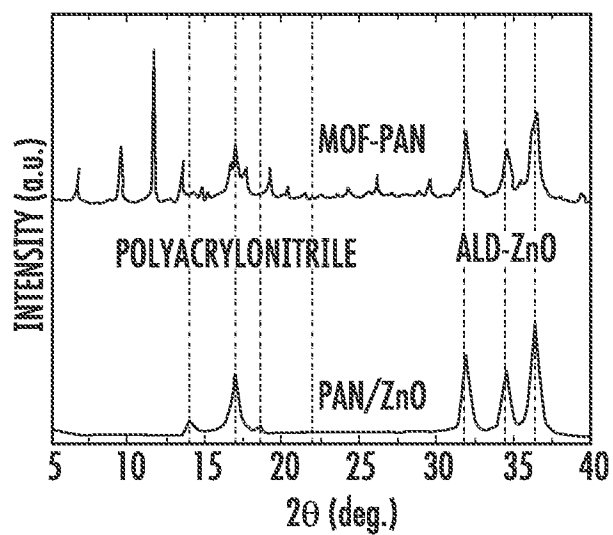


FIG. 34

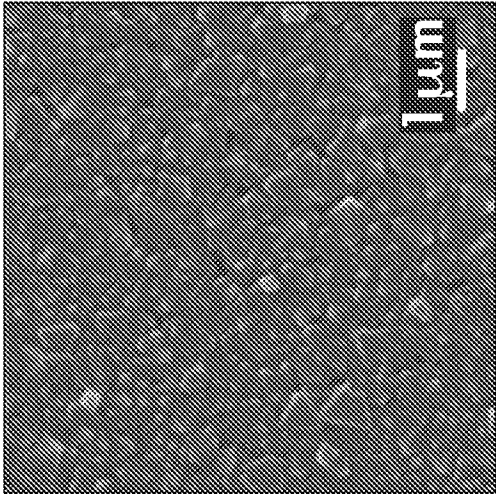


FIG. 36

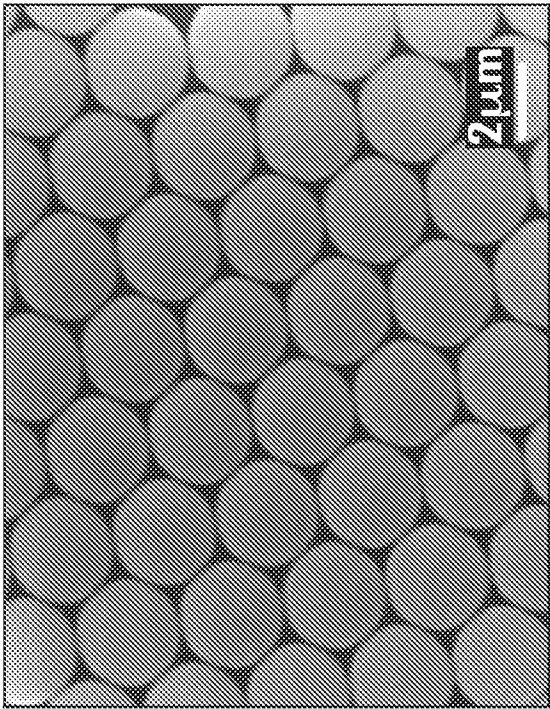


FIG. 38

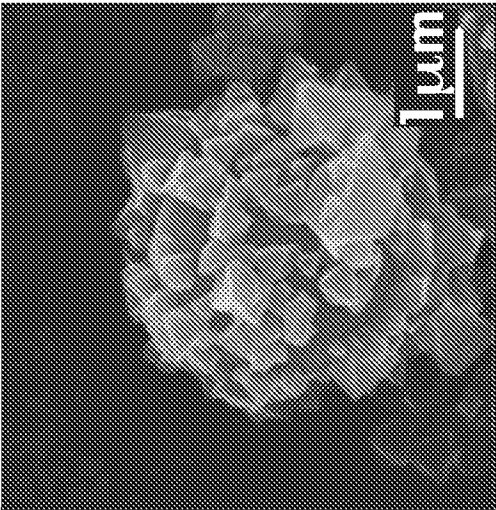


FIG. 35

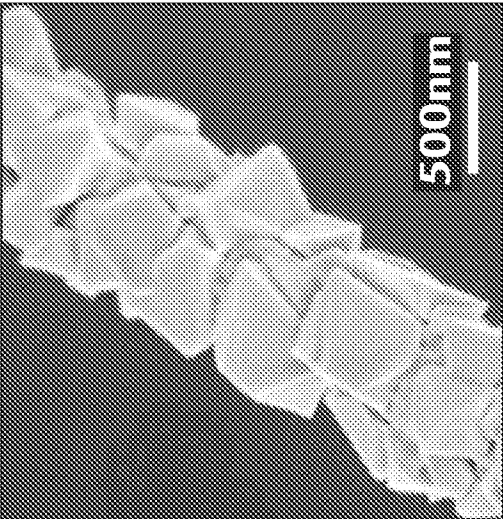


FIG. 37

16/45

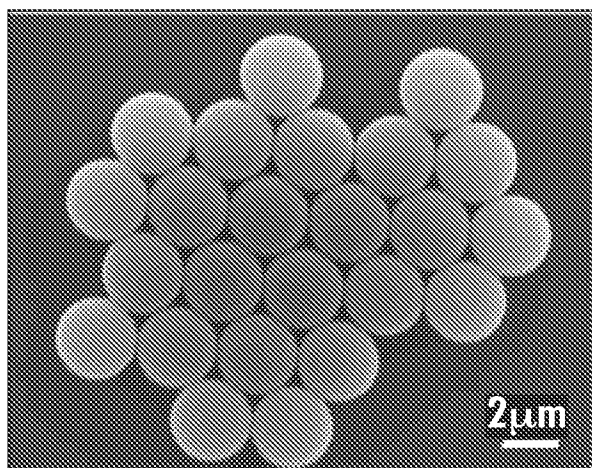


FIG. 39

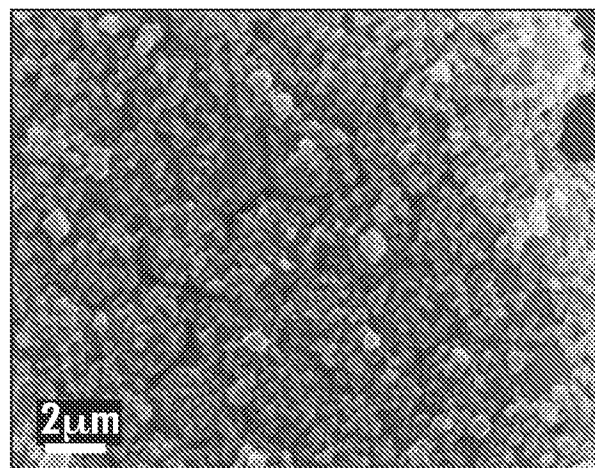


FIG. 40

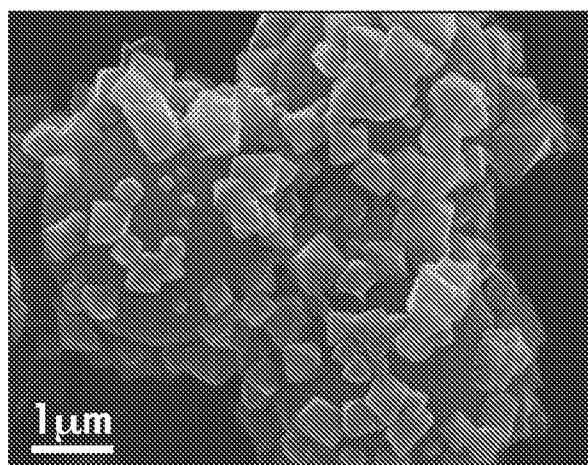


FIG. 41

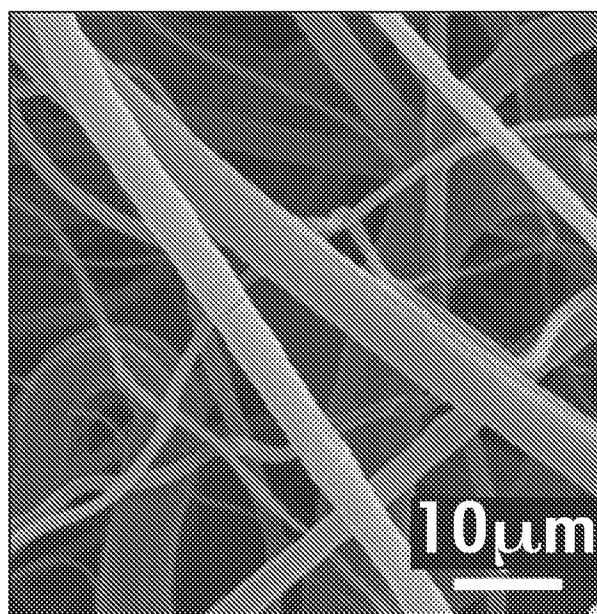


FIG. 42

17/45

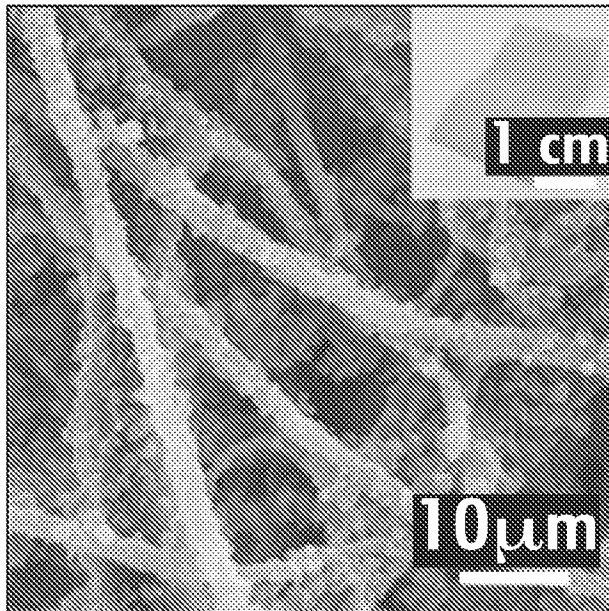


FIG. 43

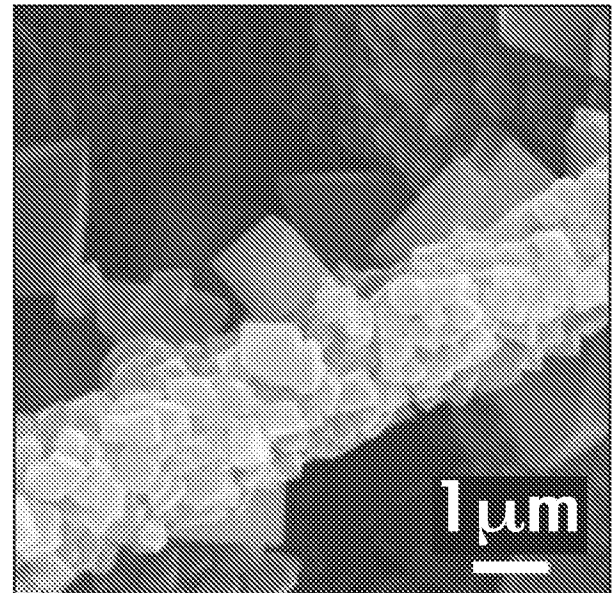


FIG. 44

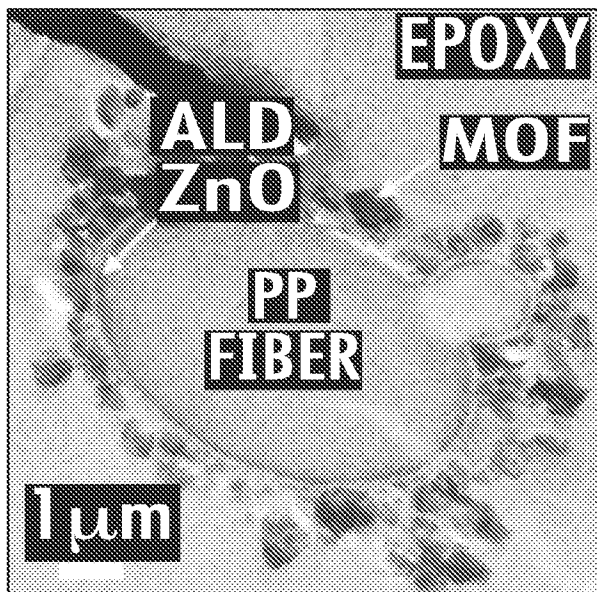


FIG. 45

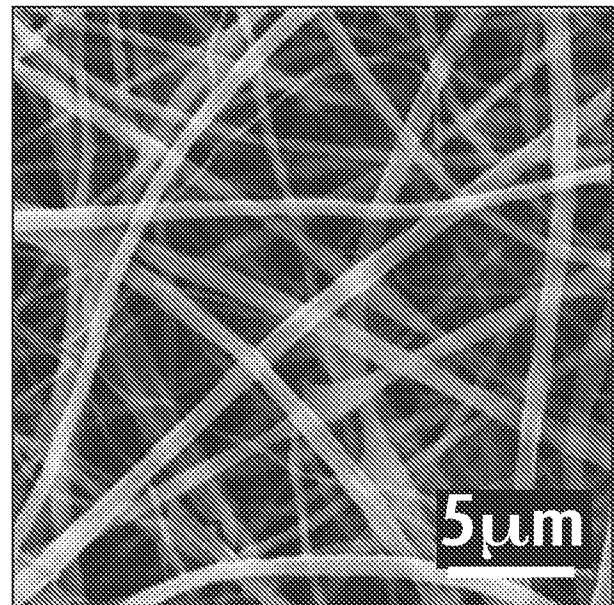


FIG. 46

18/45

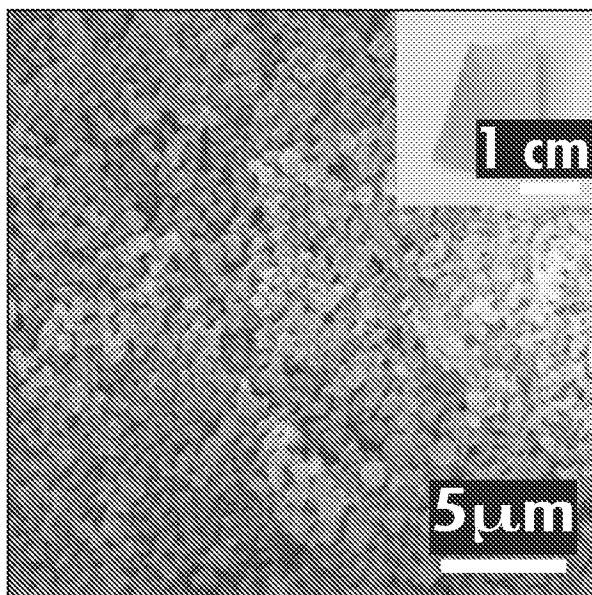


FIG. 47

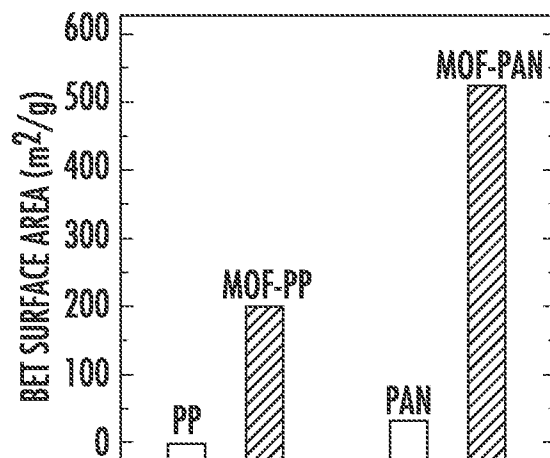


FIG. 48

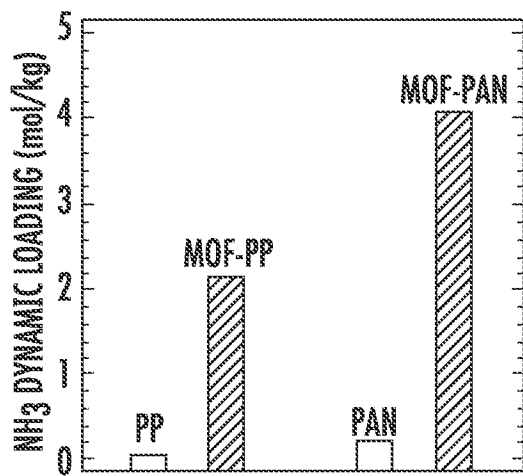


FIG. 49

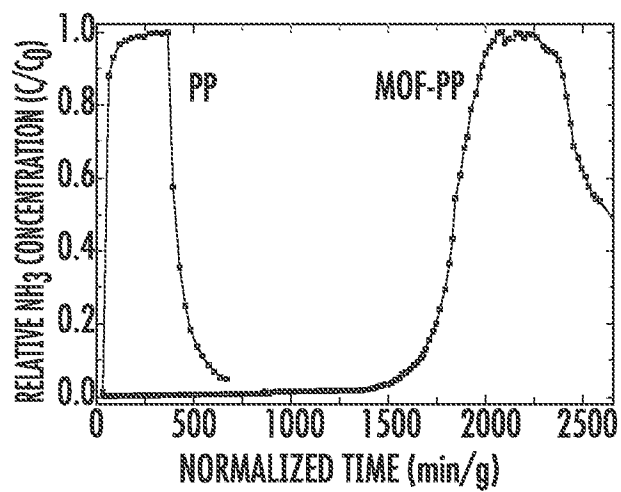


FIG. 50

19/45

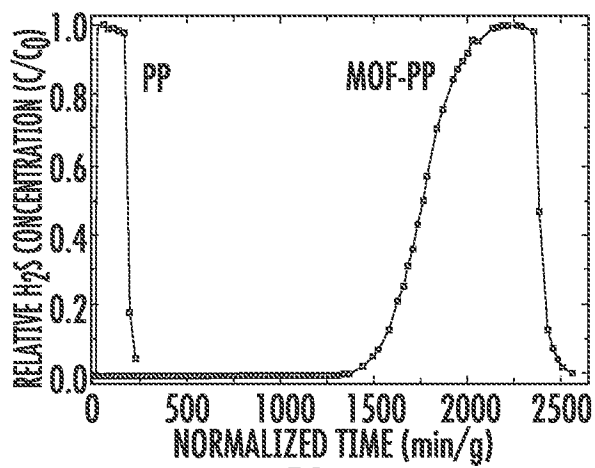


FIG. 51

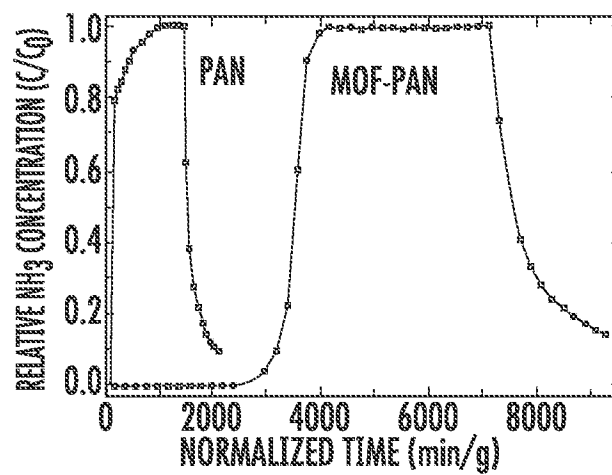


FIG. 52

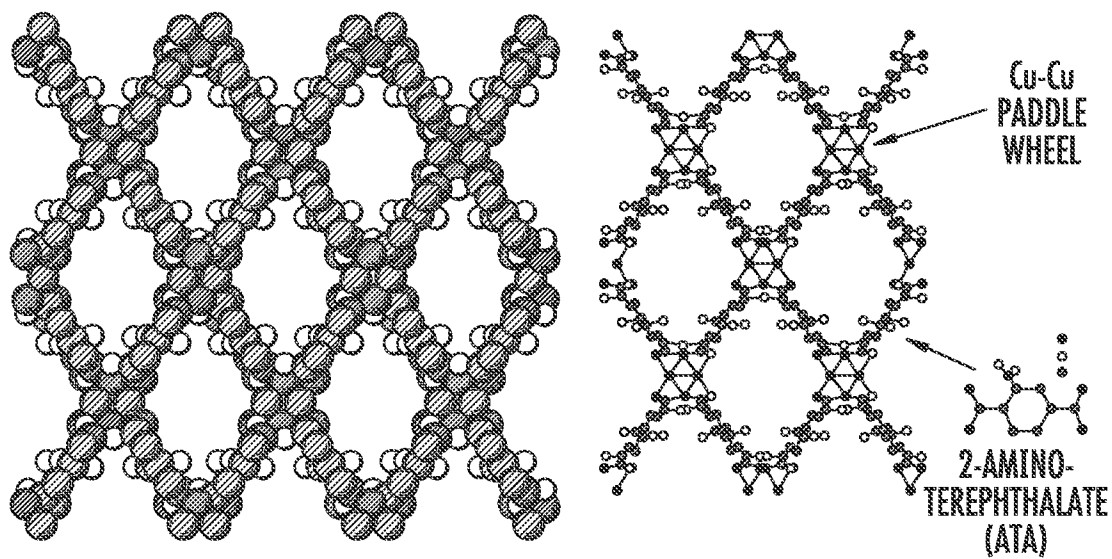
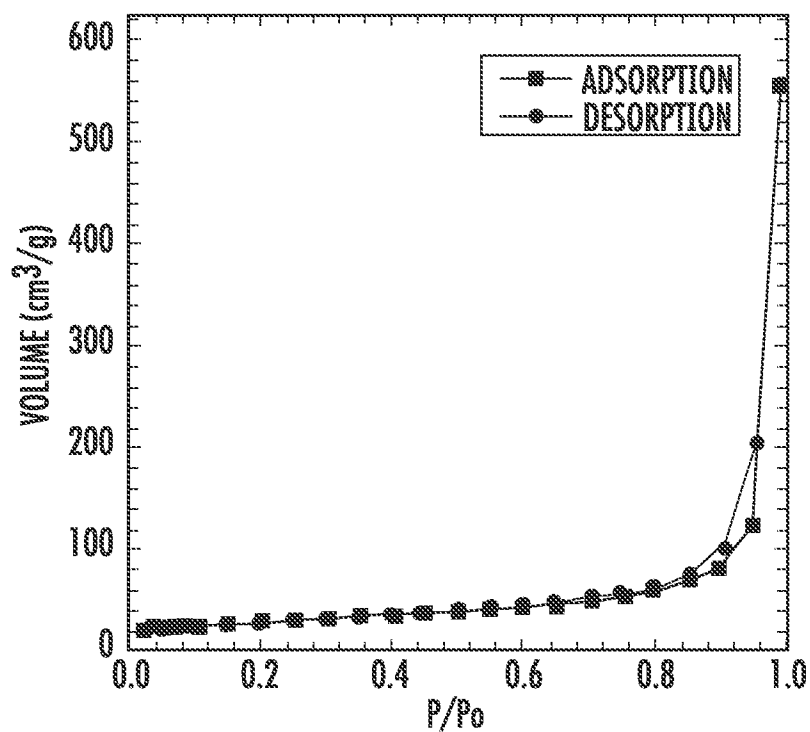
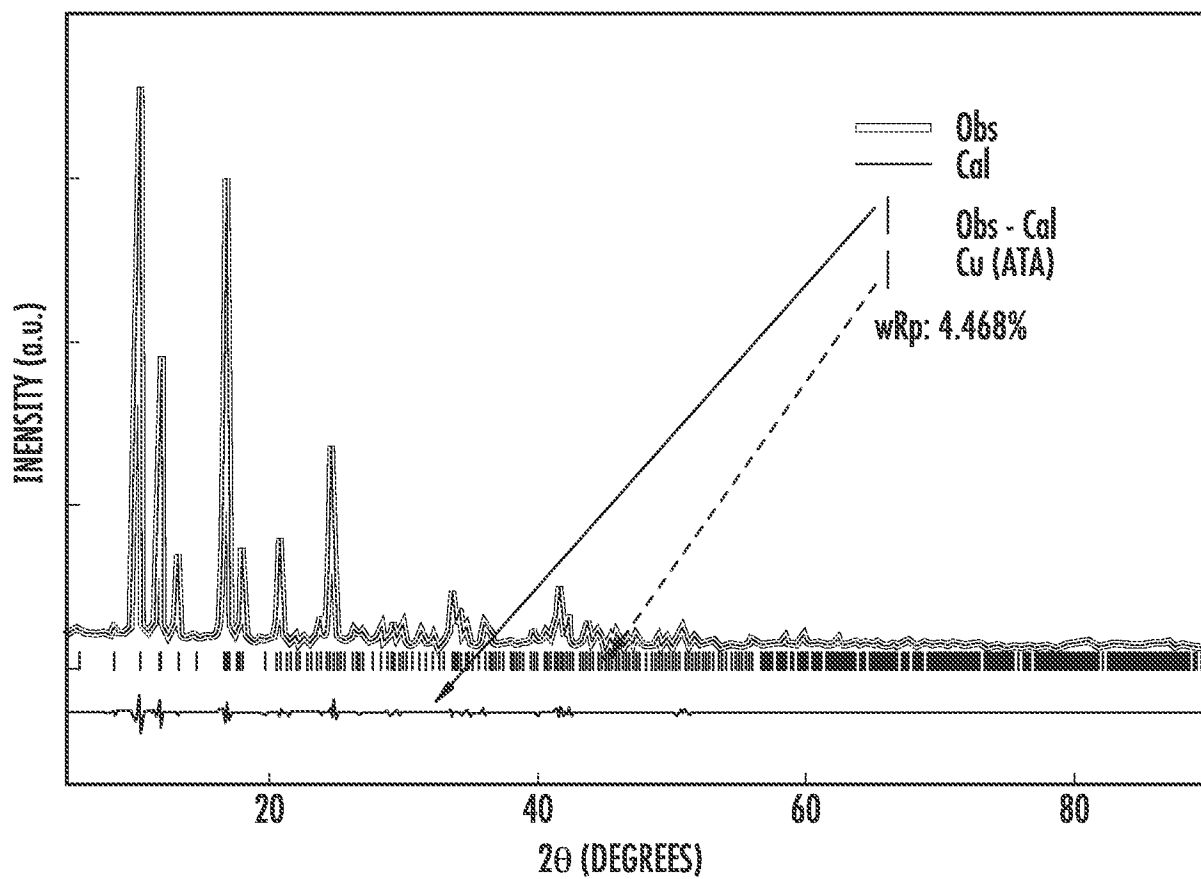


FIG. 53

20/45



21/45

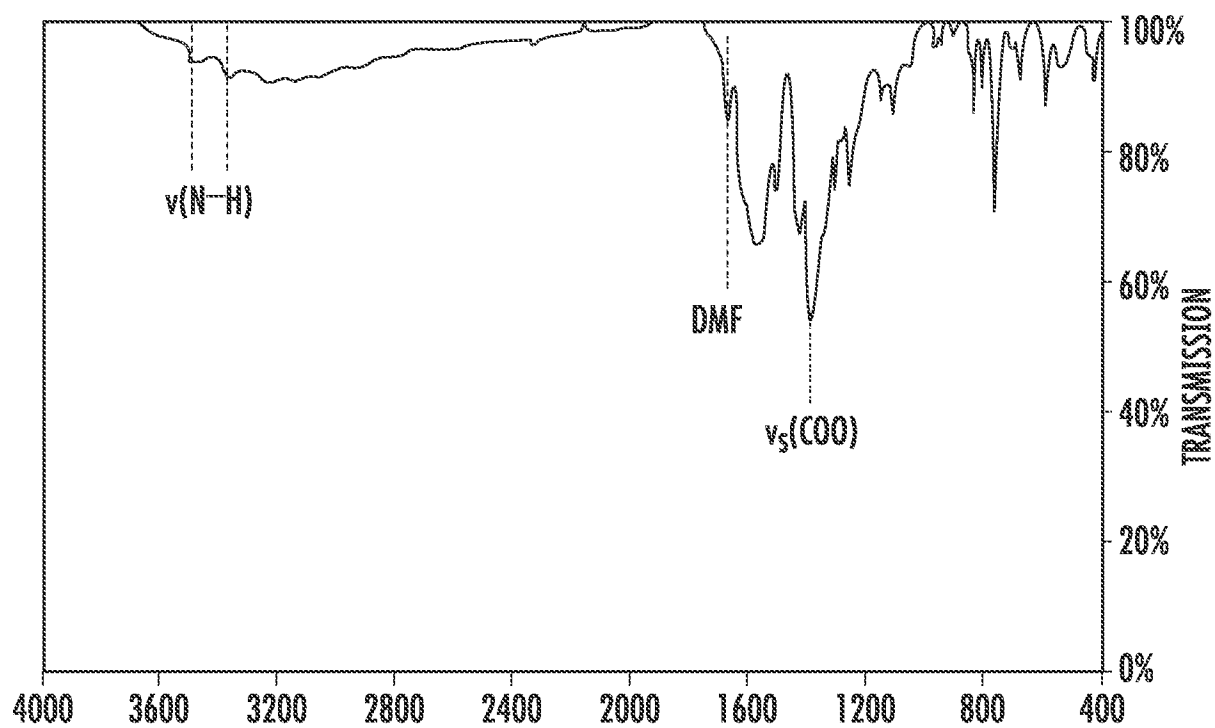


FIG. 56

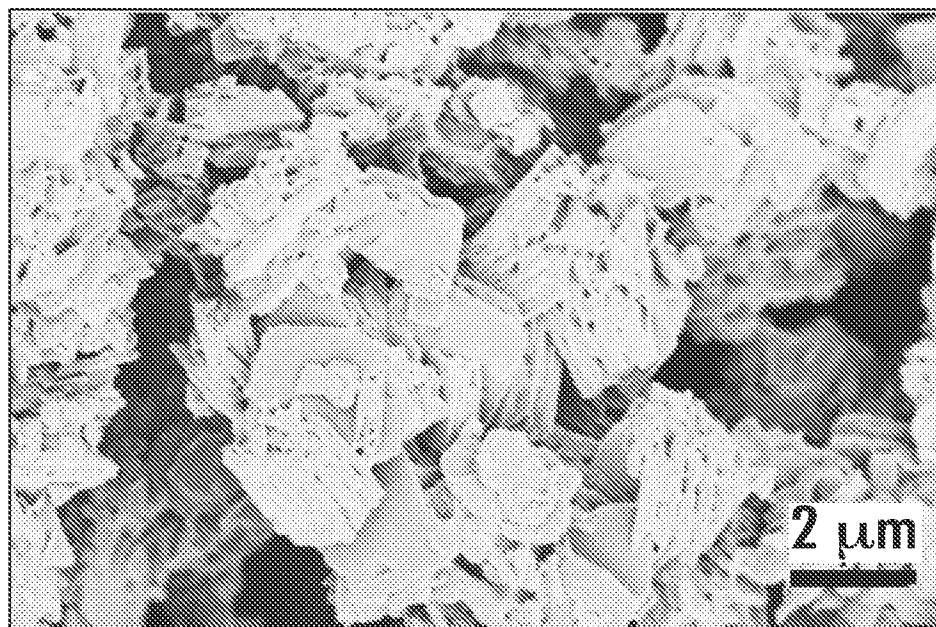


FIG. 57

22/45

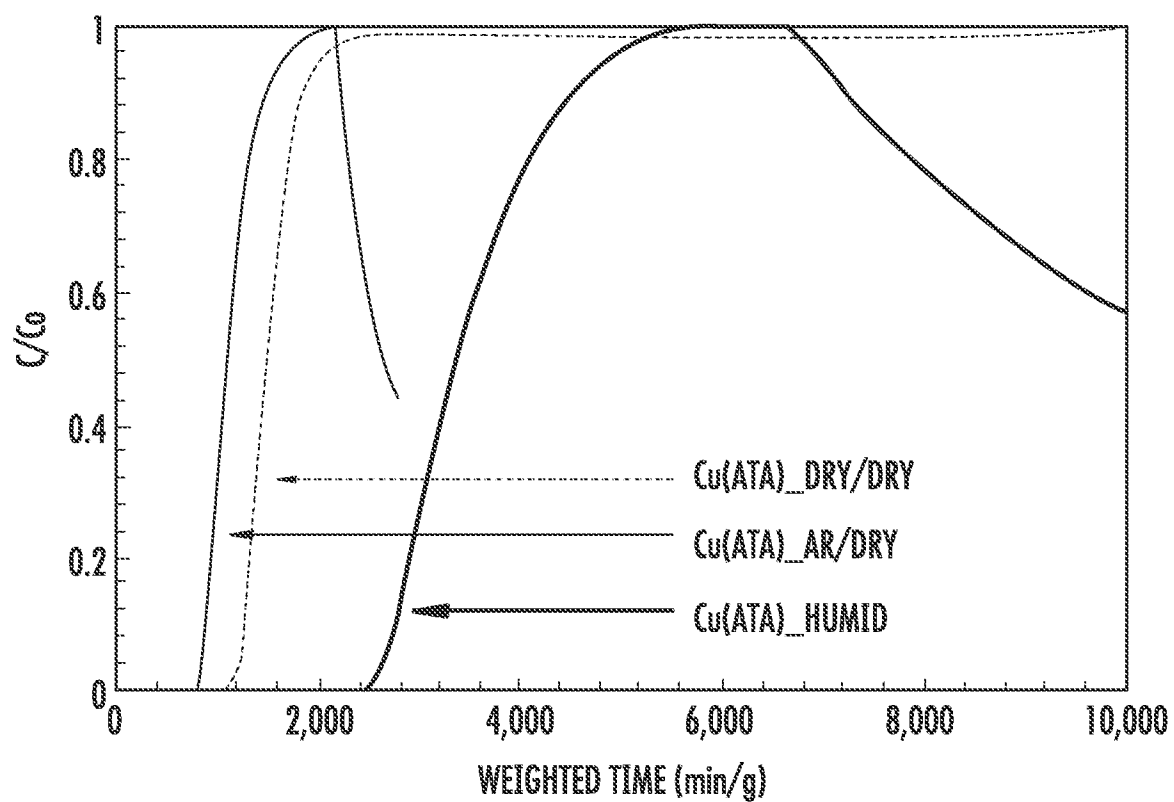


FIG. 58

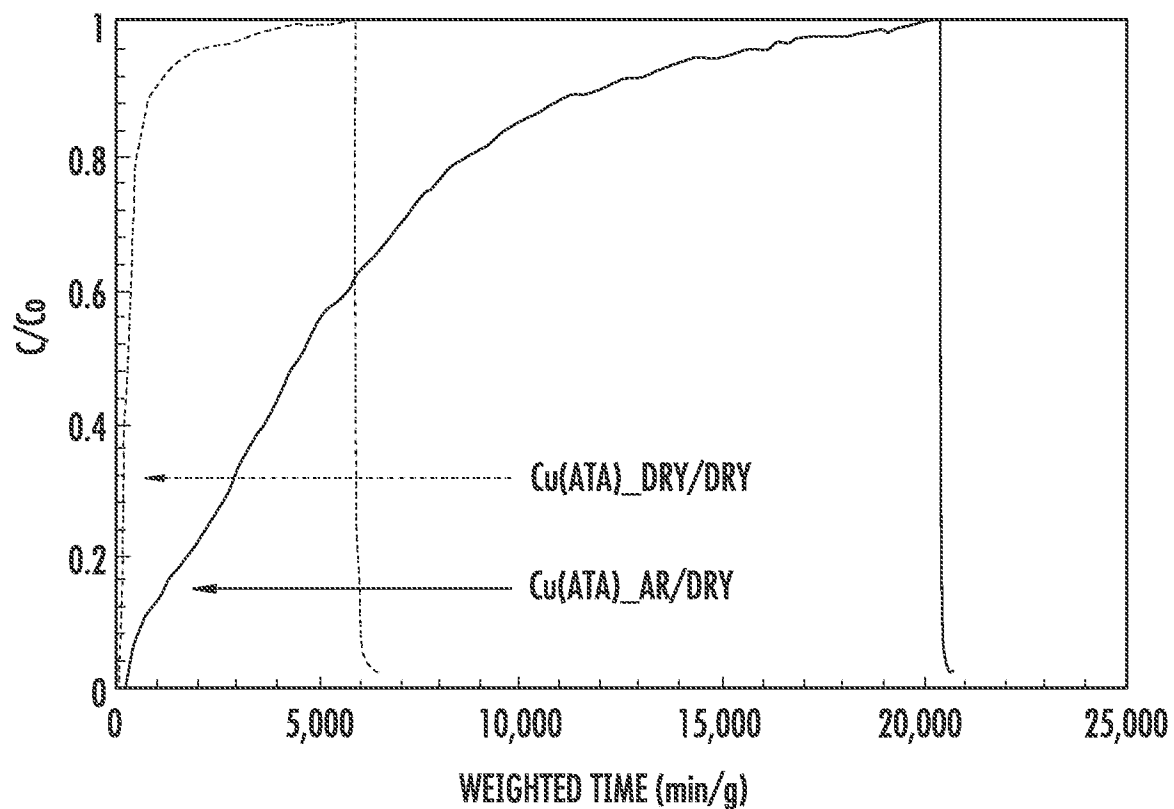


FIG. 59

23/45

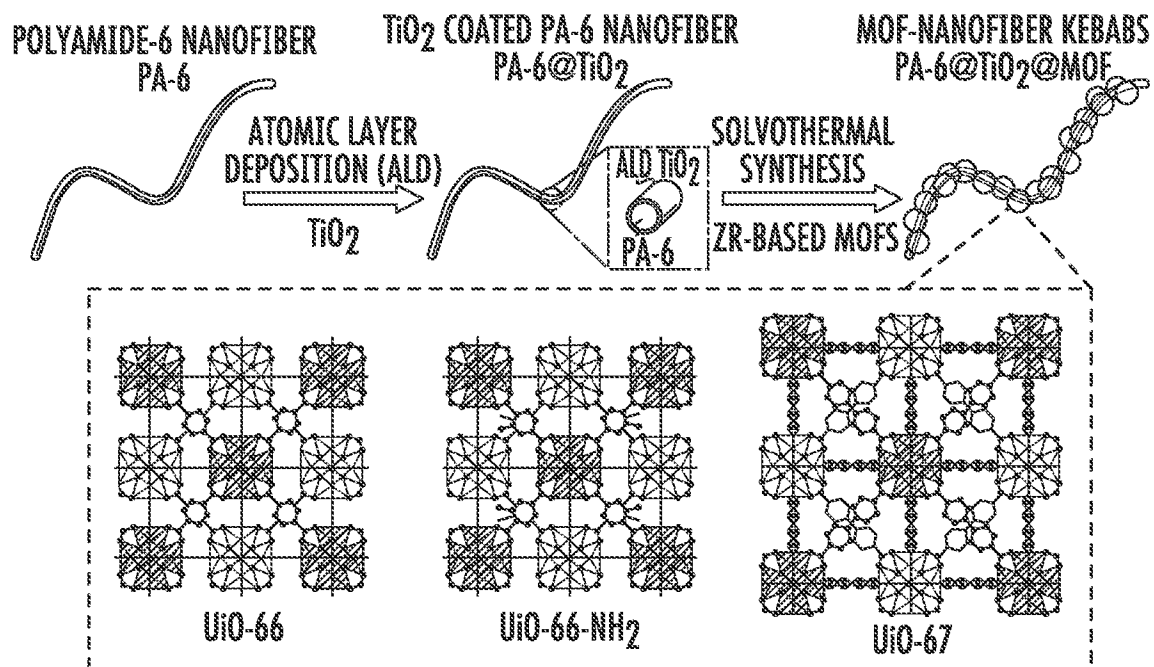


FIG. 60

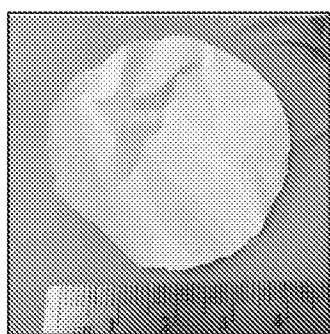


FIG. 61A

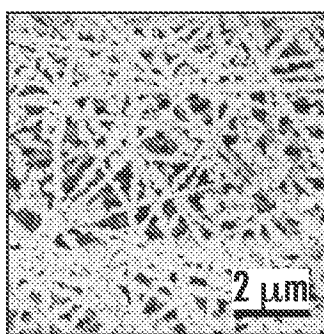


FIG. 61B

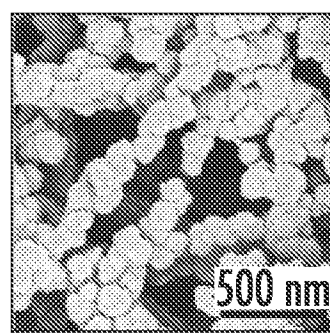


FIG. 61C

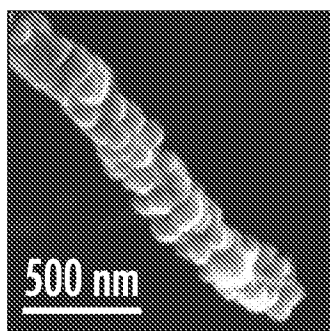


FIG. 61D

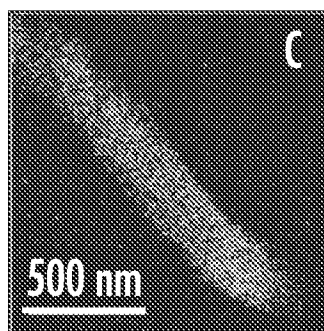


FIG. 61E

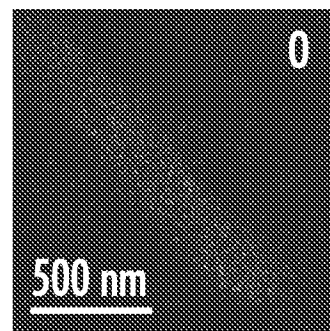


FIG. 61F

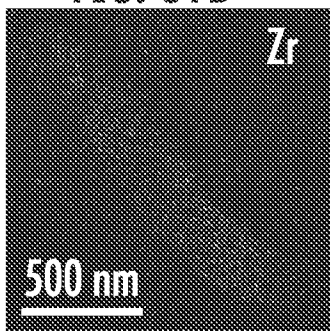


FIG. 61G

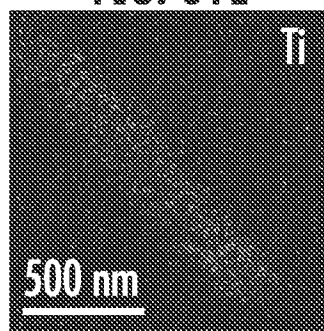


FIG. 61H

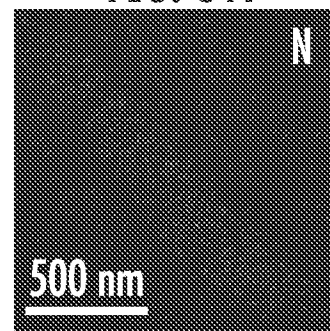


FIG. 61I

24/45

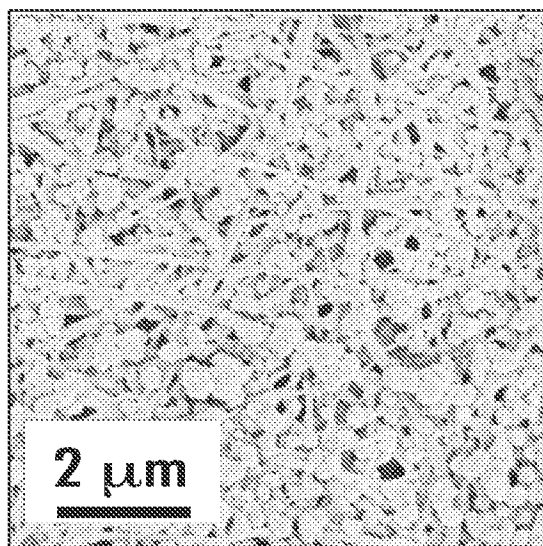


FIG. 62A

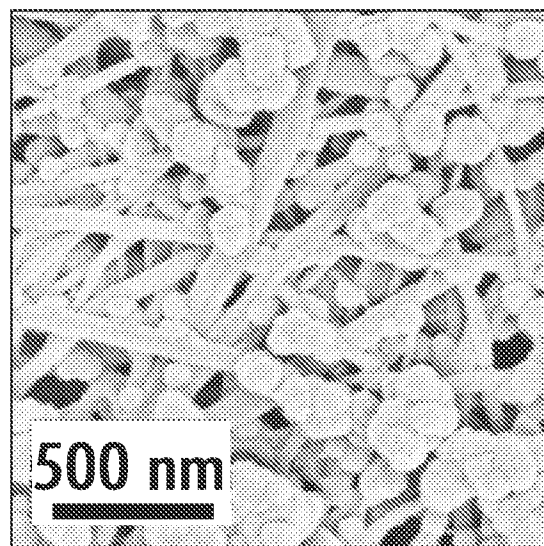


FIG. 62B

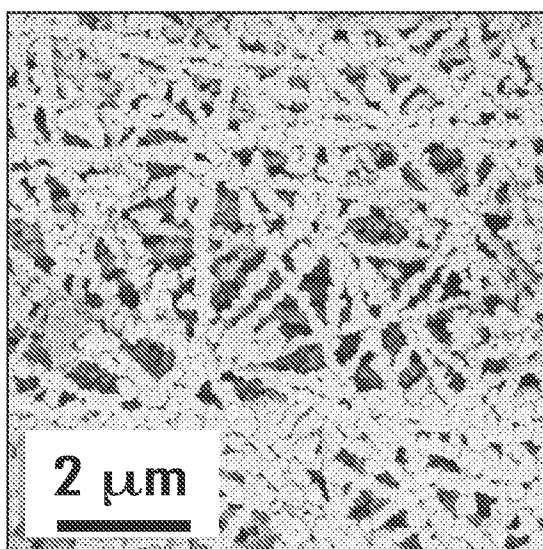


FIG. 62C

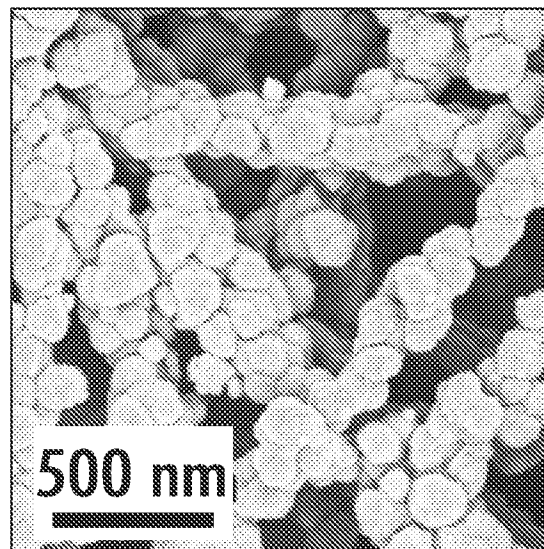


FIG. 62D

25/45

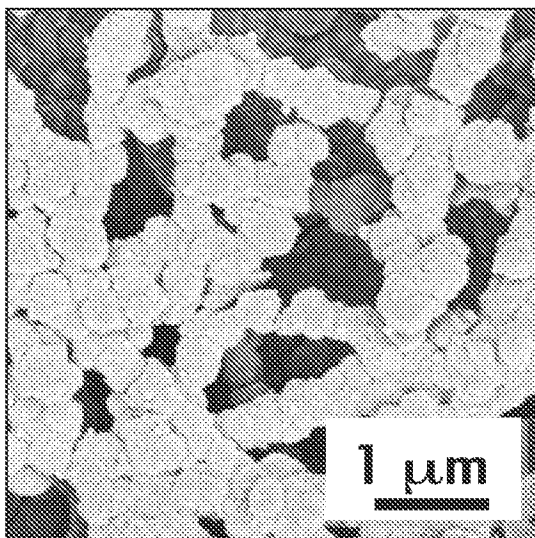


FIG. 63A

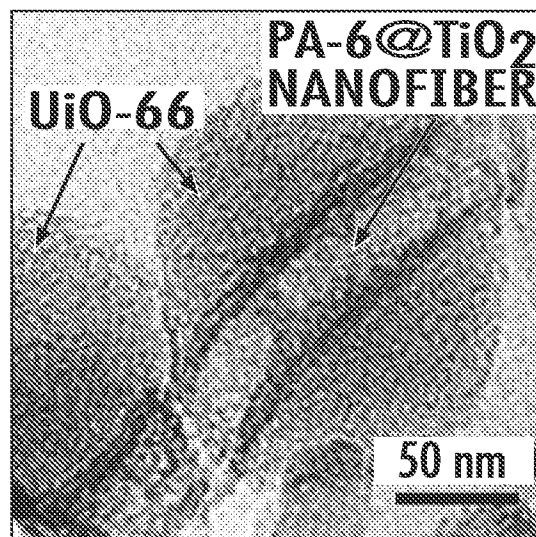


FIG. 63B

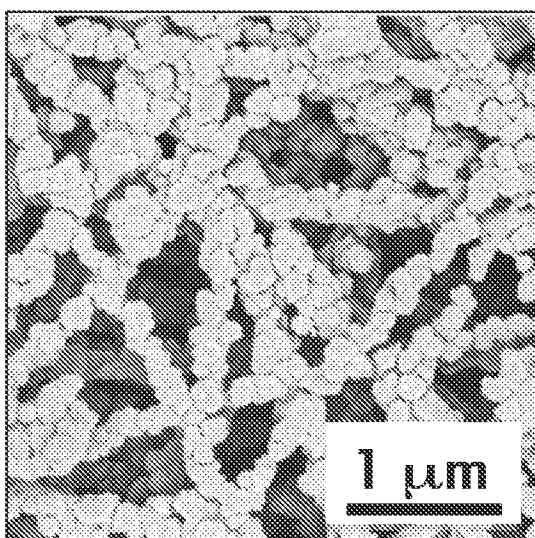


FIG. 63C

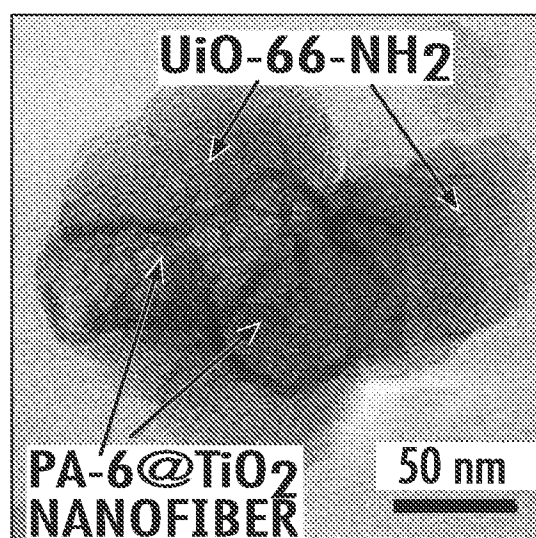


FIG. 63D

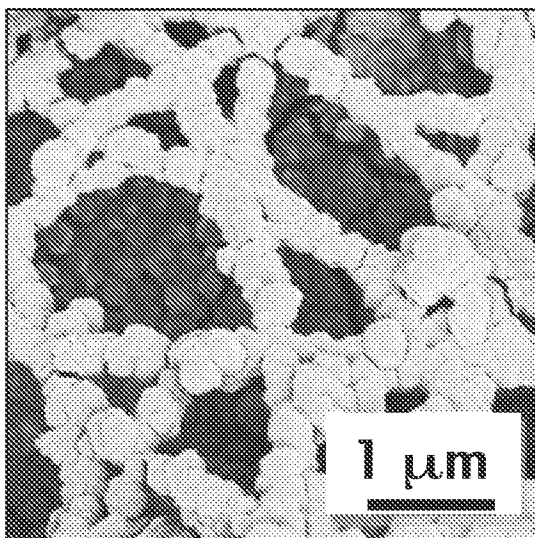


FIG. 63E

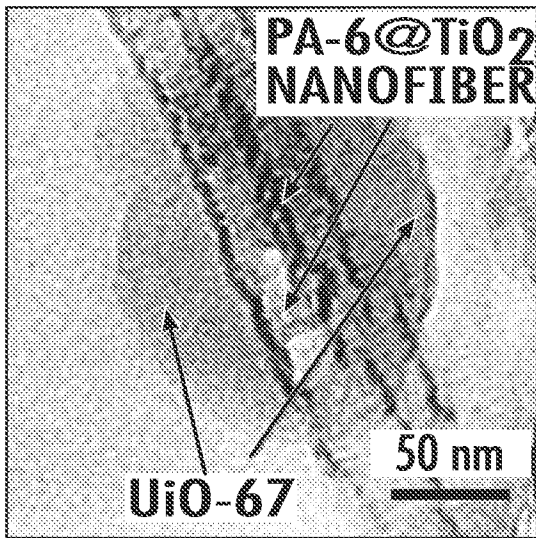


FIG. 63F

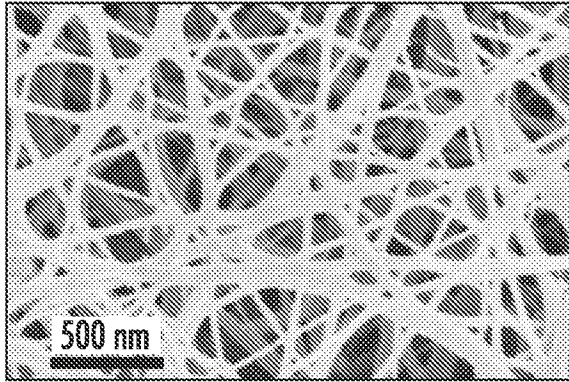


FIG. 64A

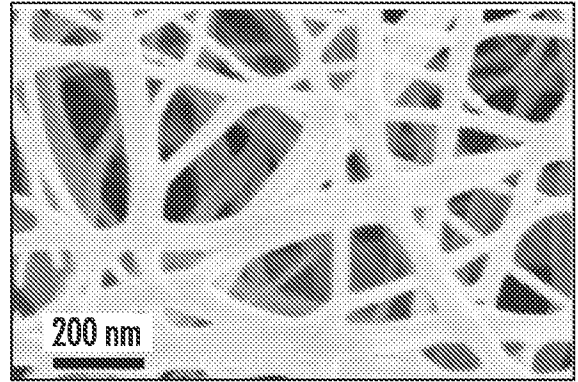


FIG. 64B

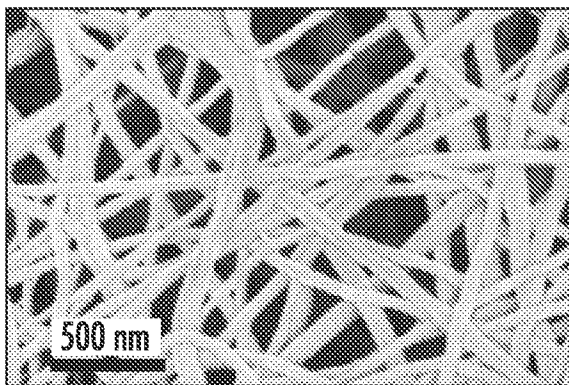


FIG. 64C

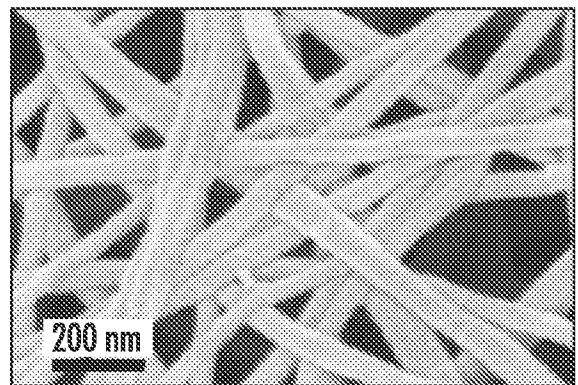
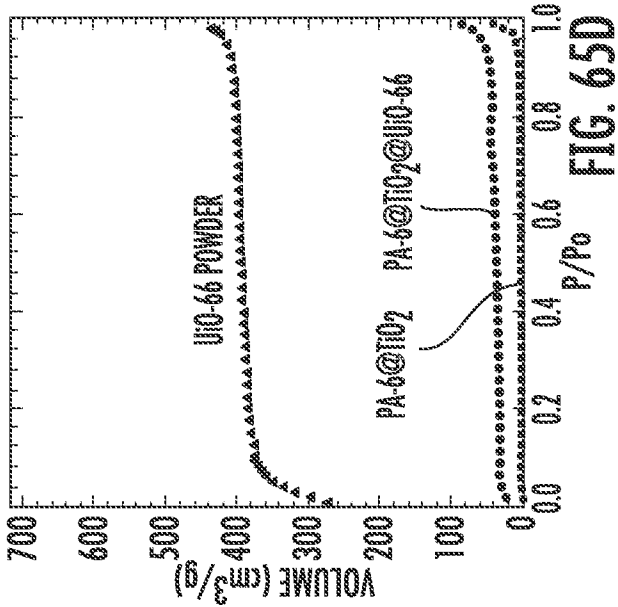
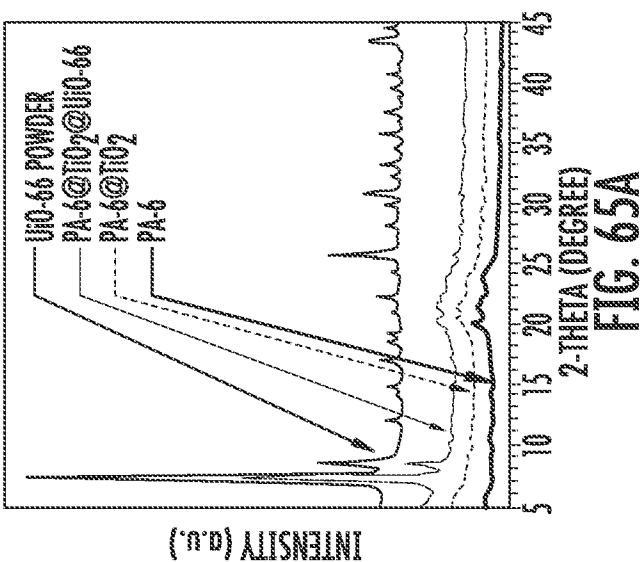
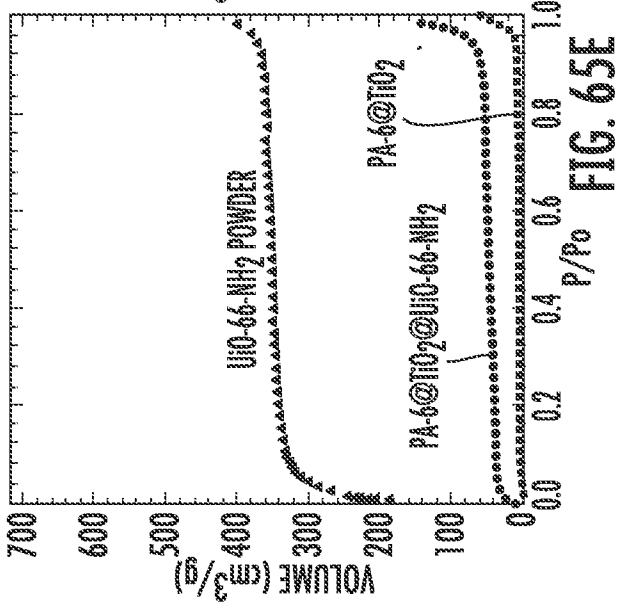
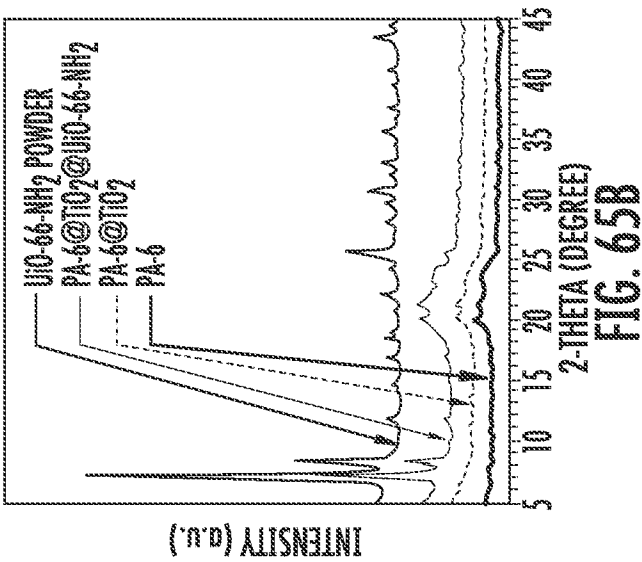
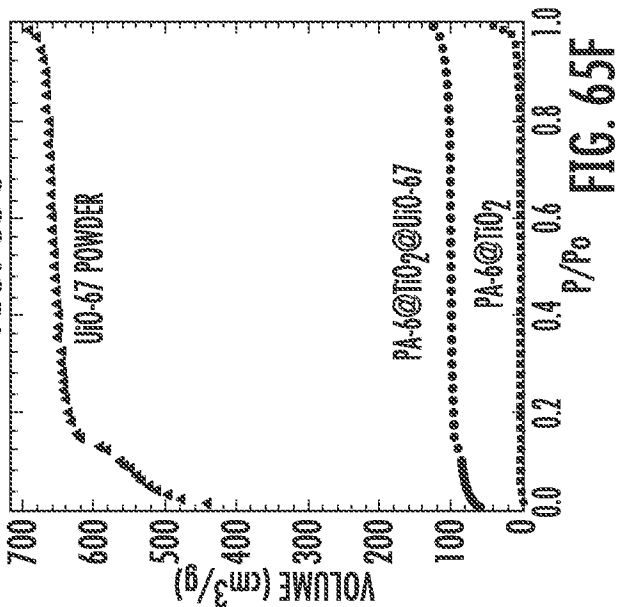
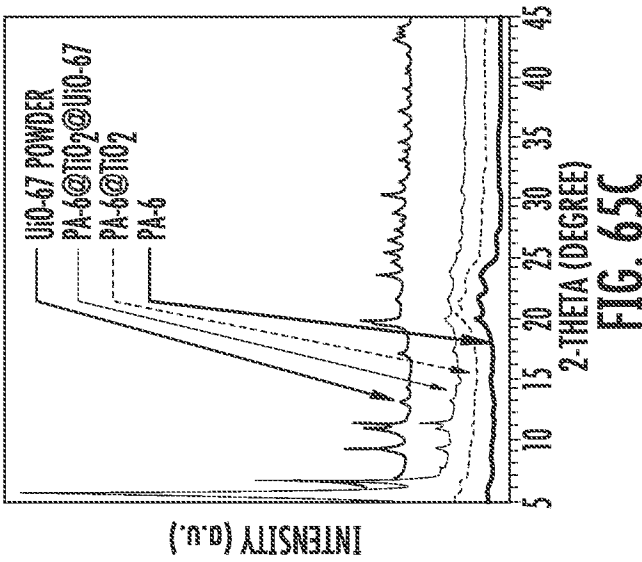


FIG. 64D



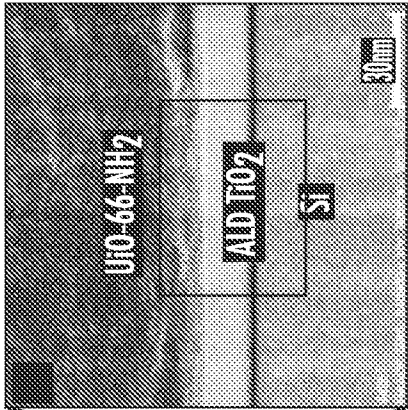


FIG. 66C

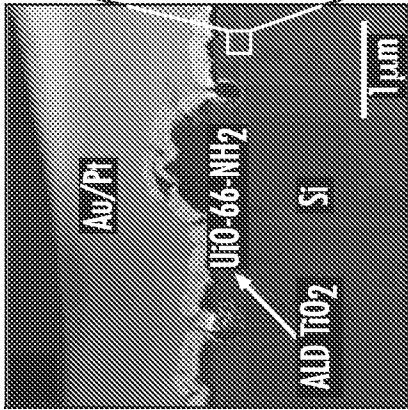


FIG. 66B

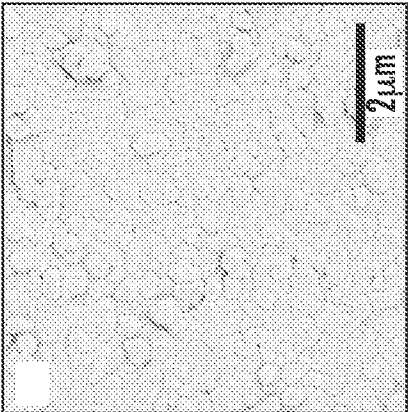


FIG. 66A

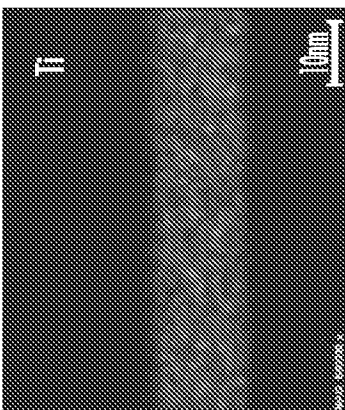


FIG. 66F

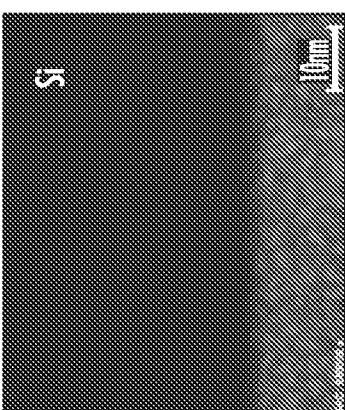


FIG. 66E

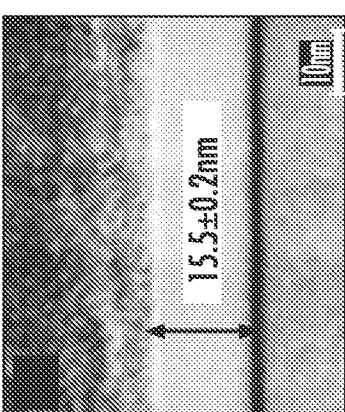


FIG. 66D

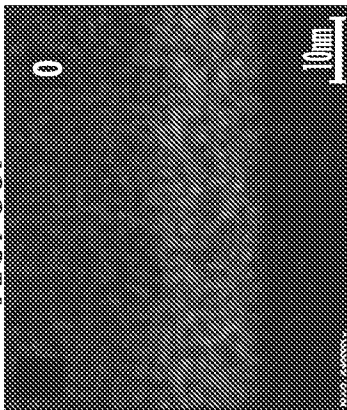


FIG. 66I

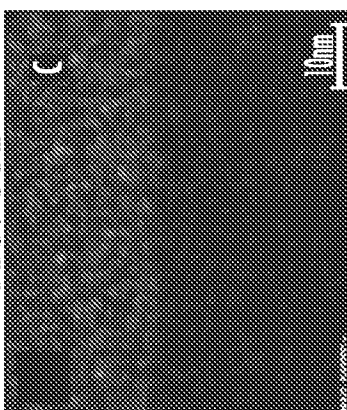


FIG. 66H

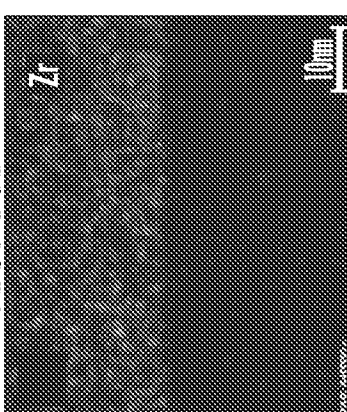


FIG. 66G

29/45

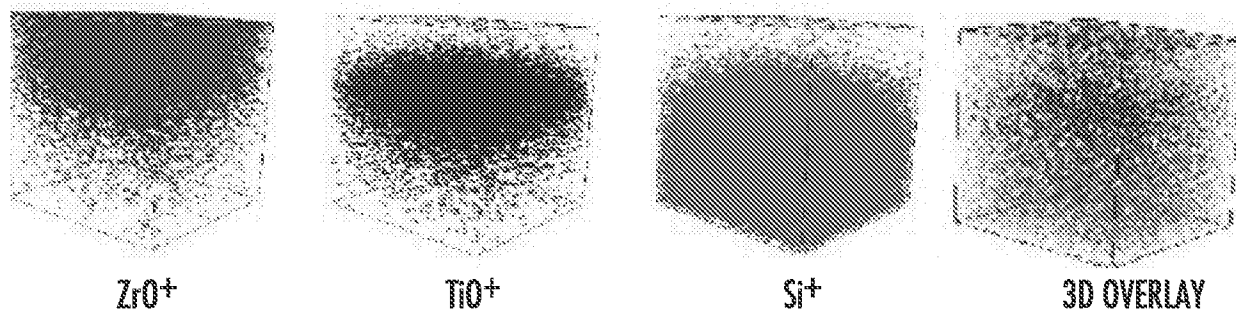
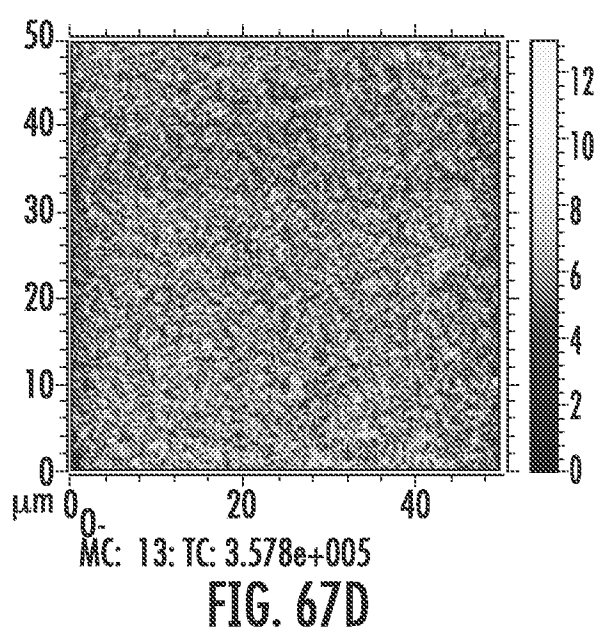
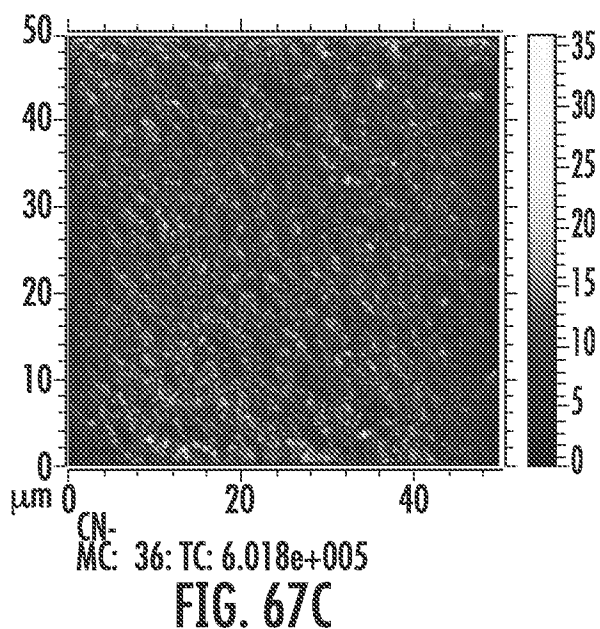
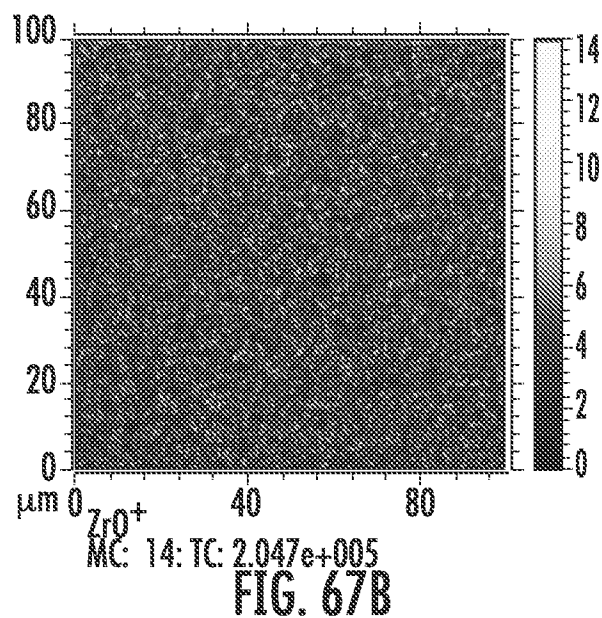
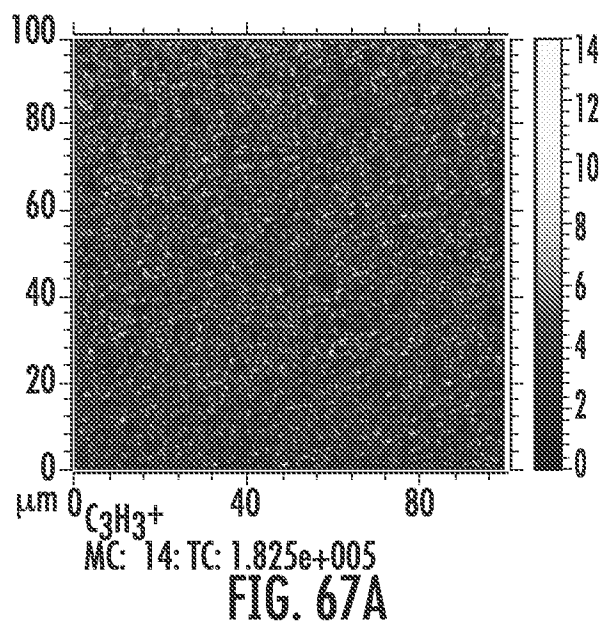


FIG. 67E

30/45

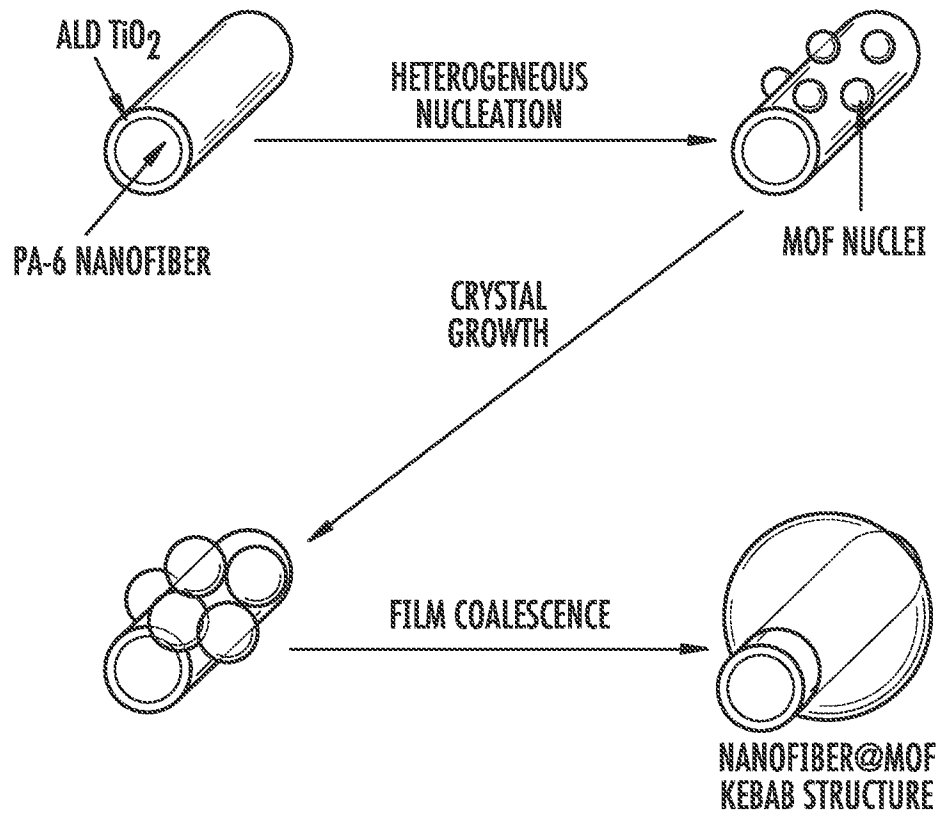
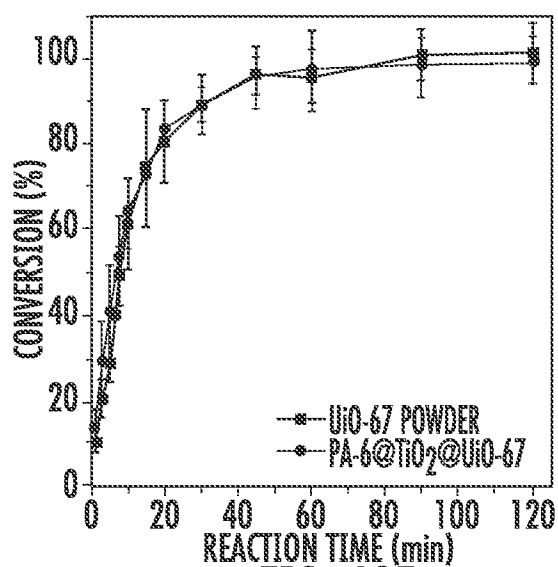
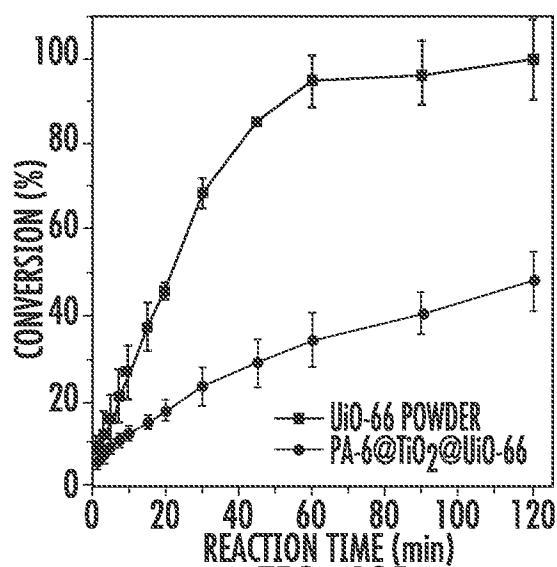
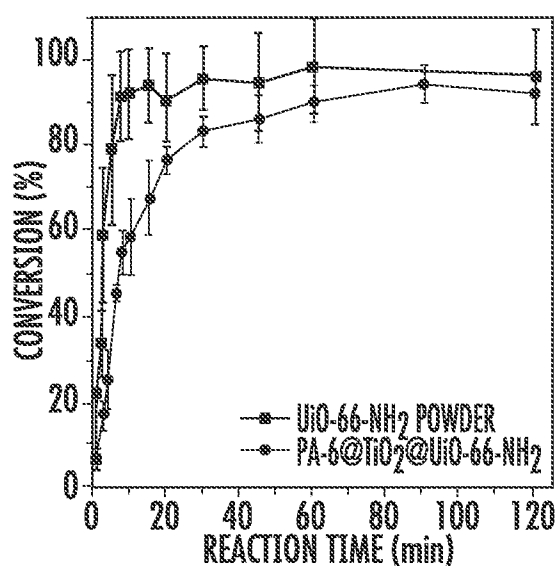
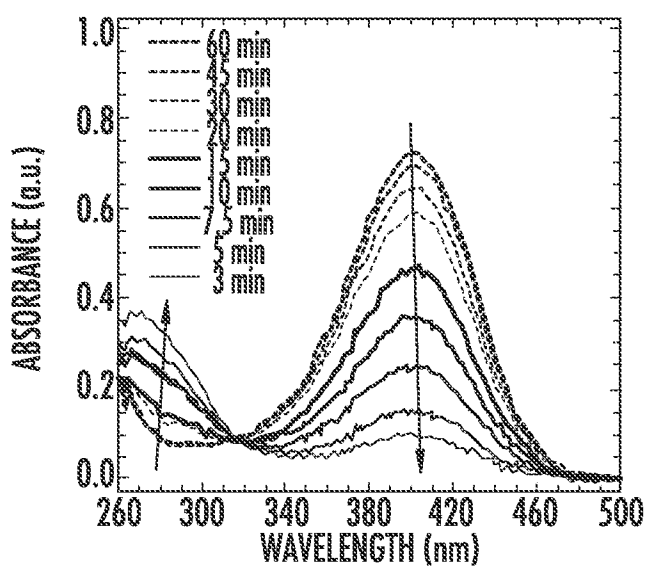
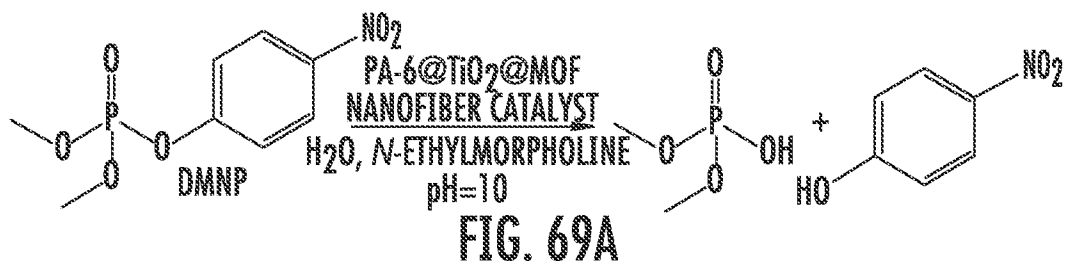


FIG. 68

31/45



32/45

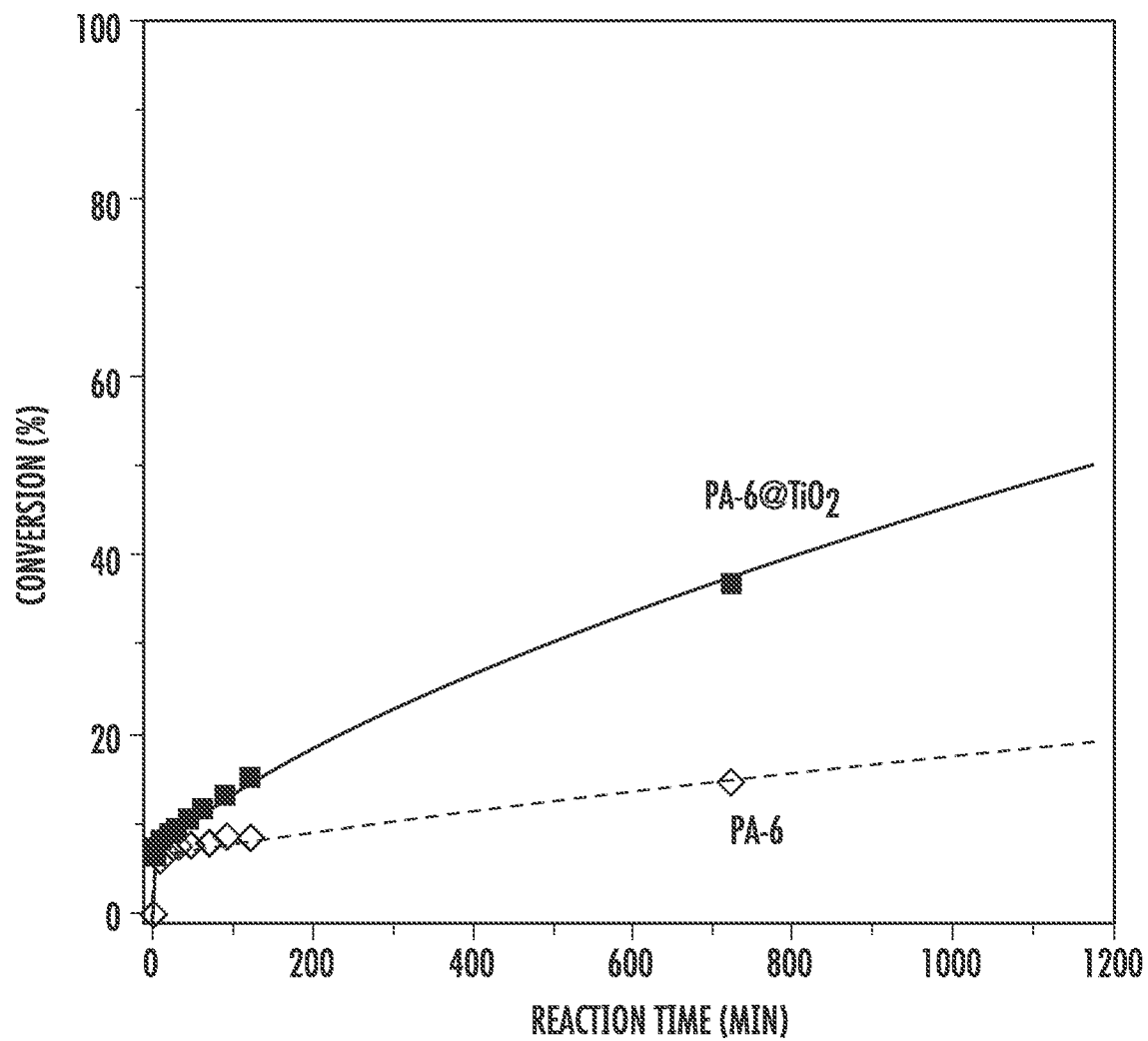


FIG. 70

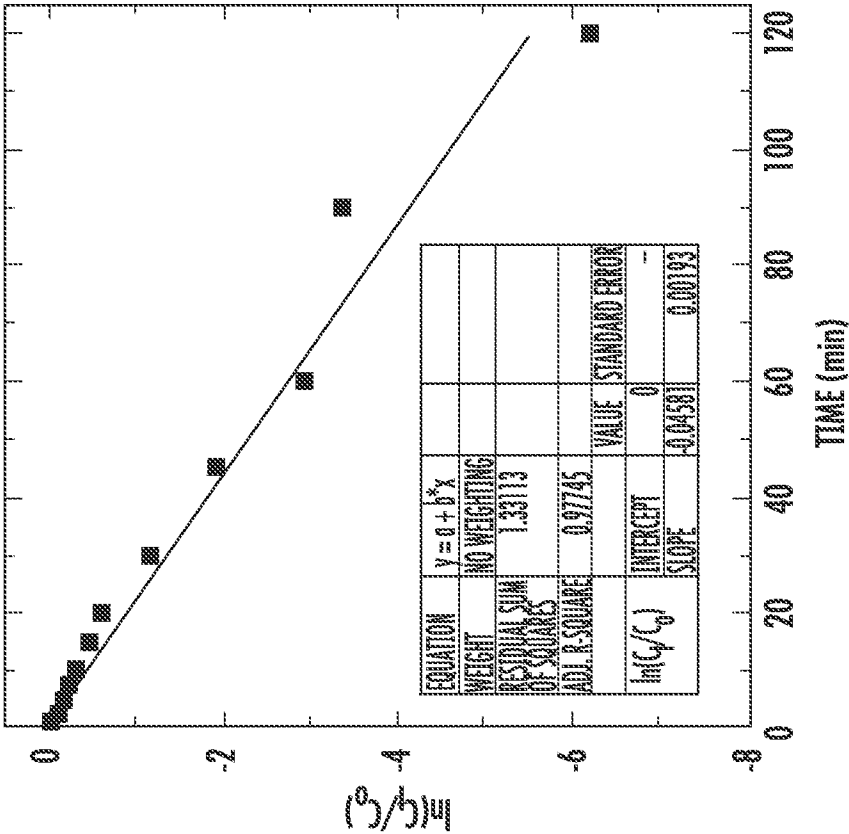


FIG. 71B

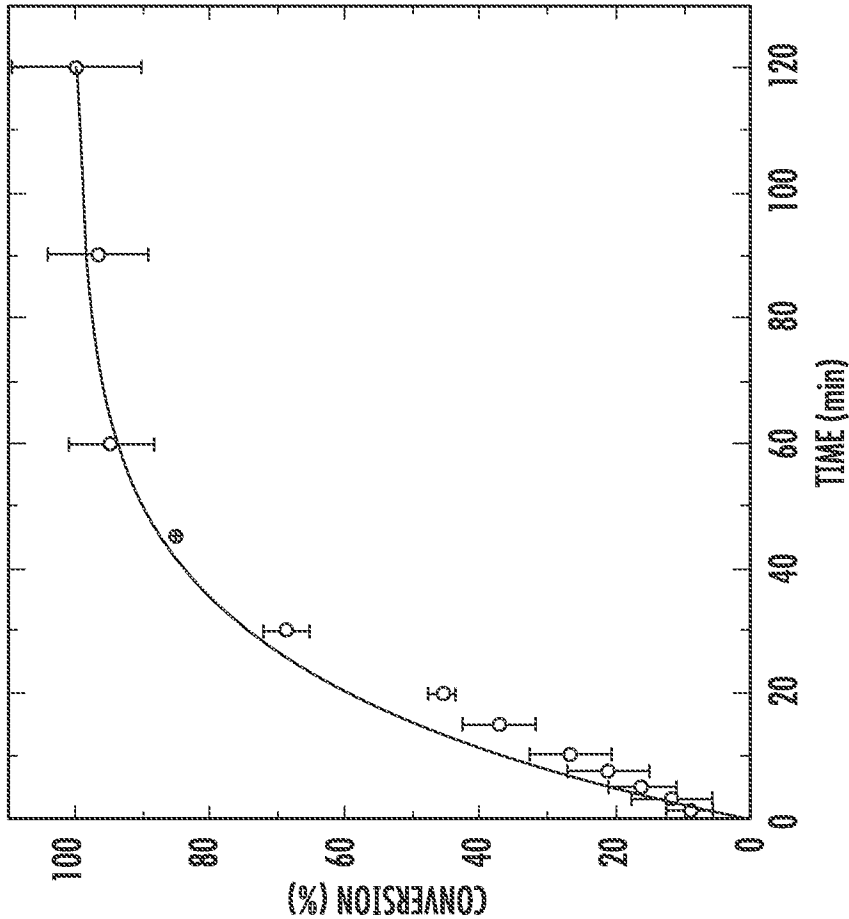
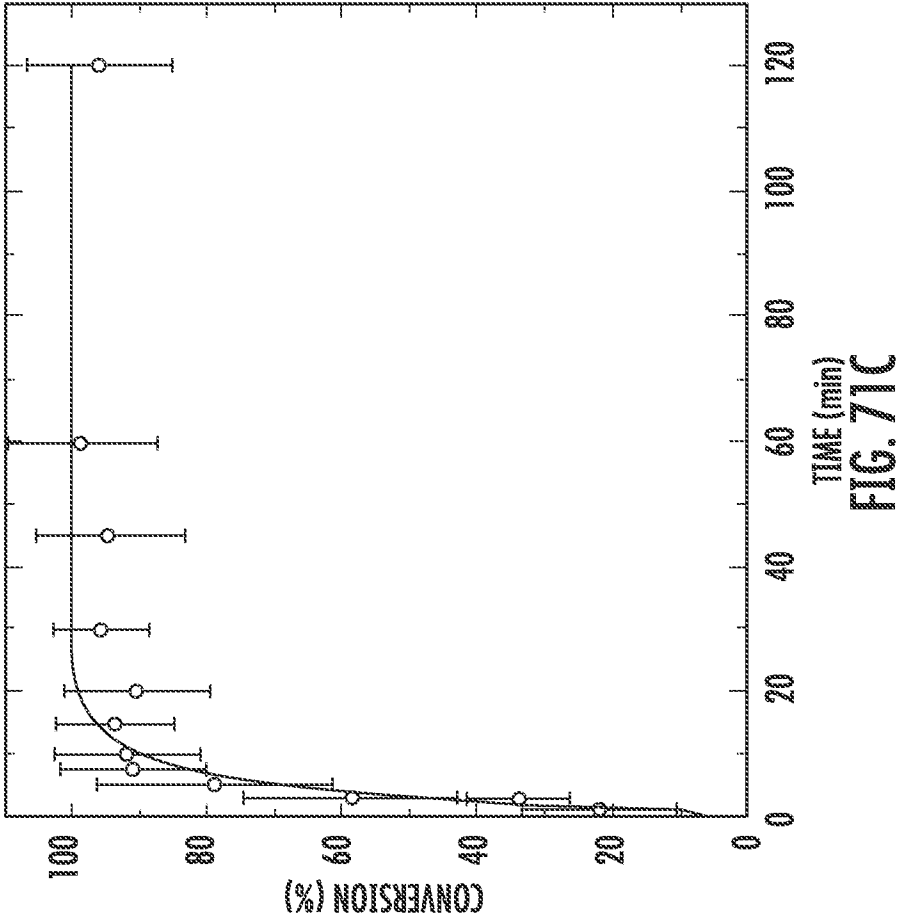
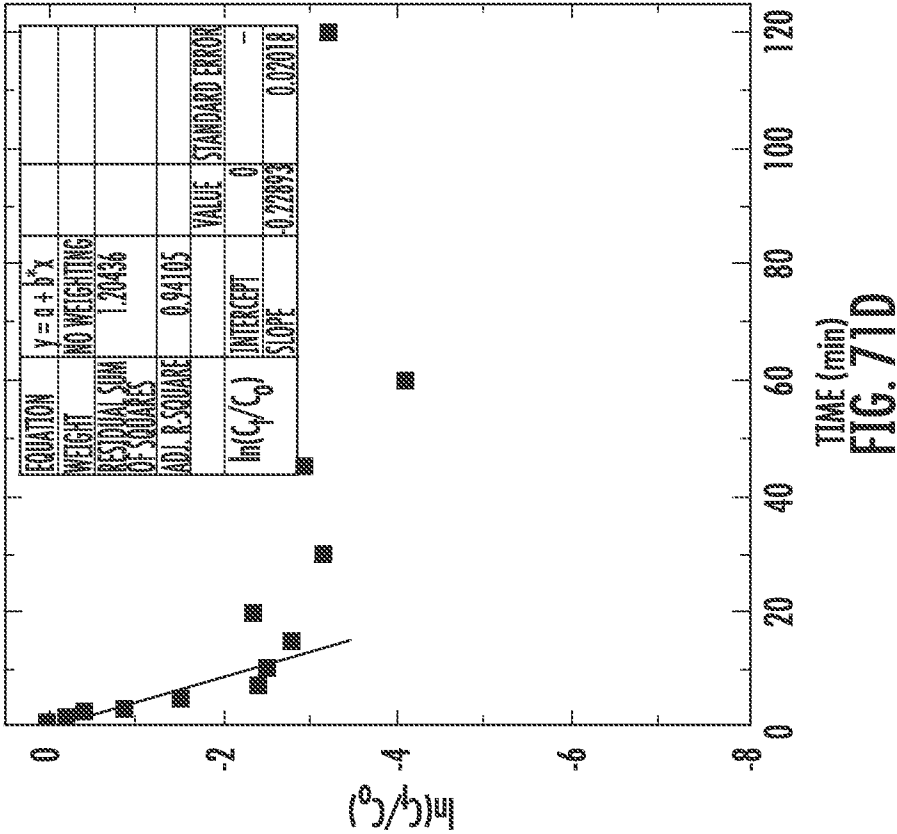
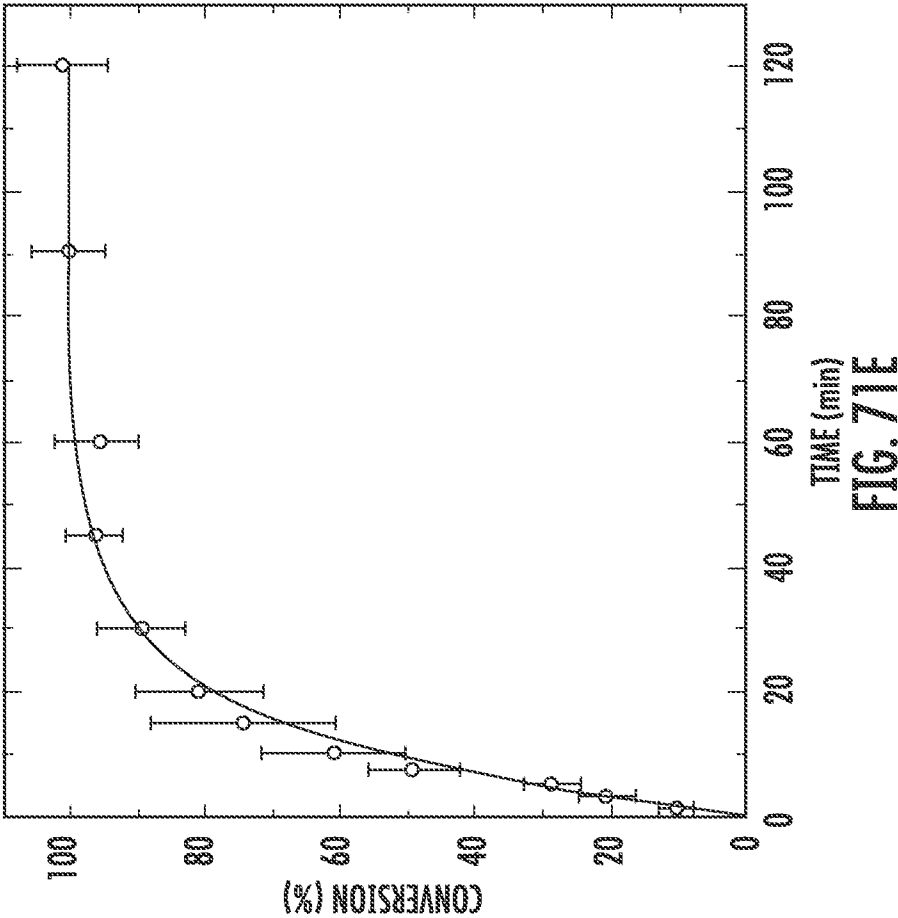
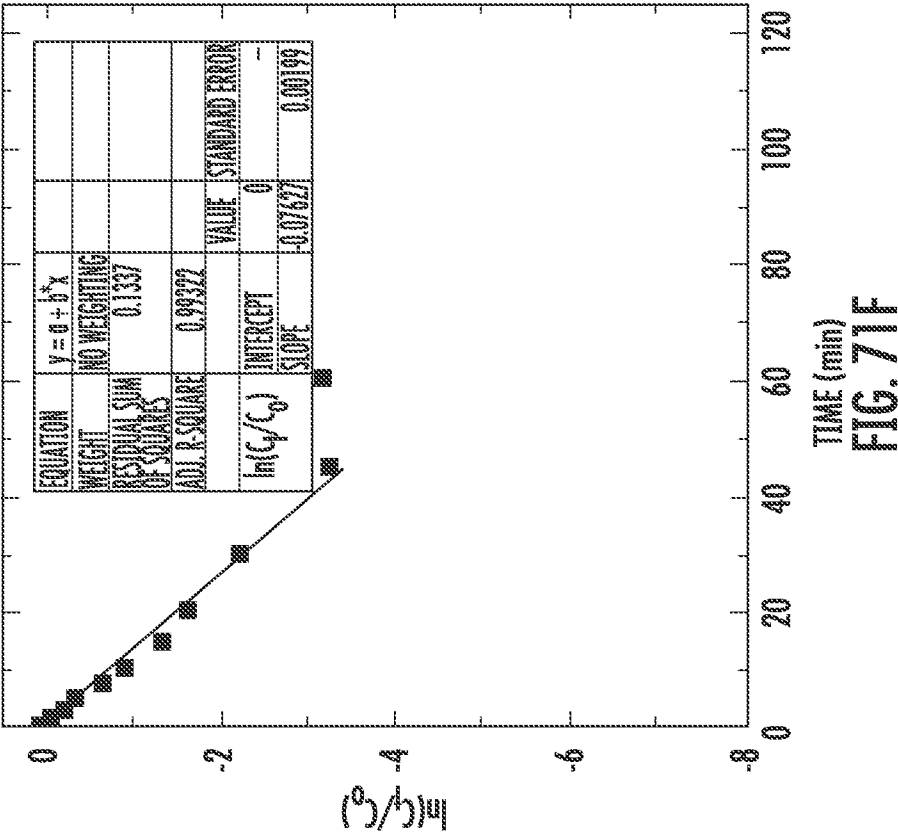
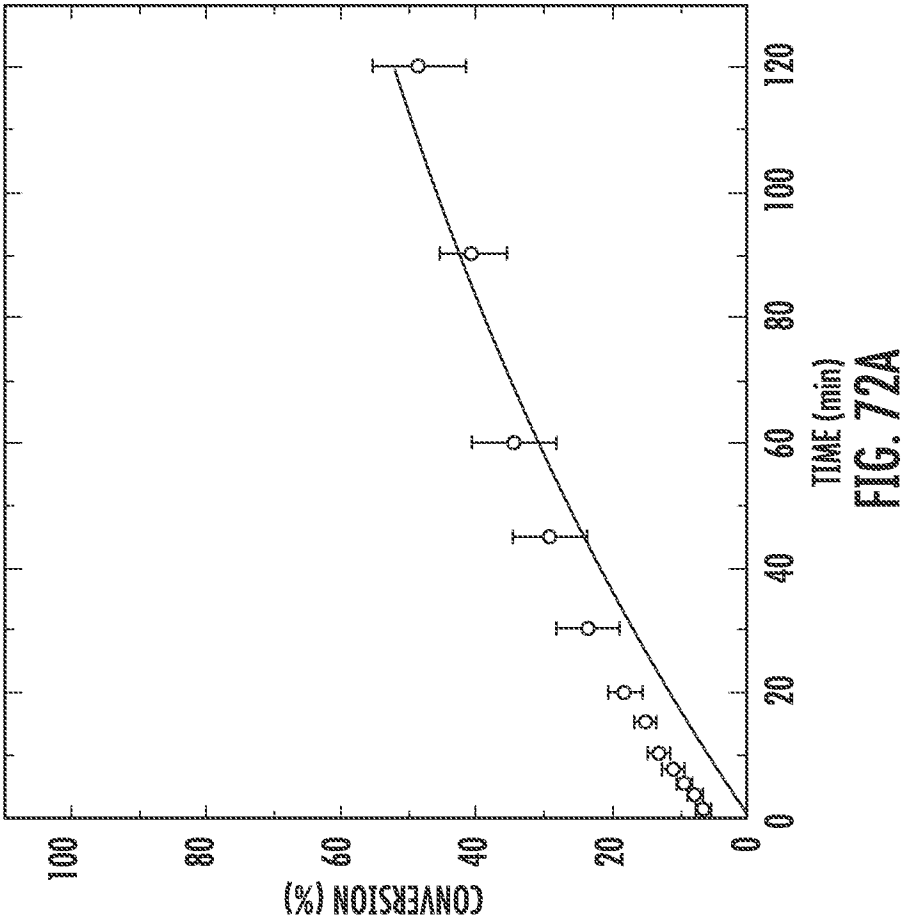
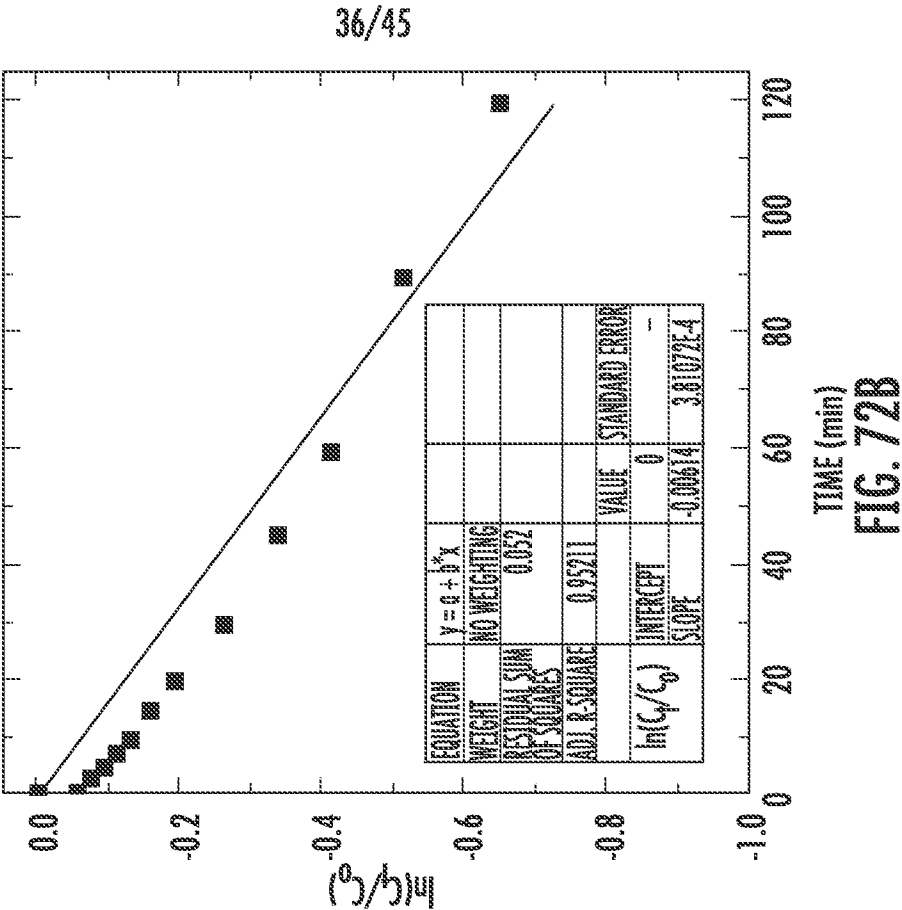


FIG. 71A







37/45

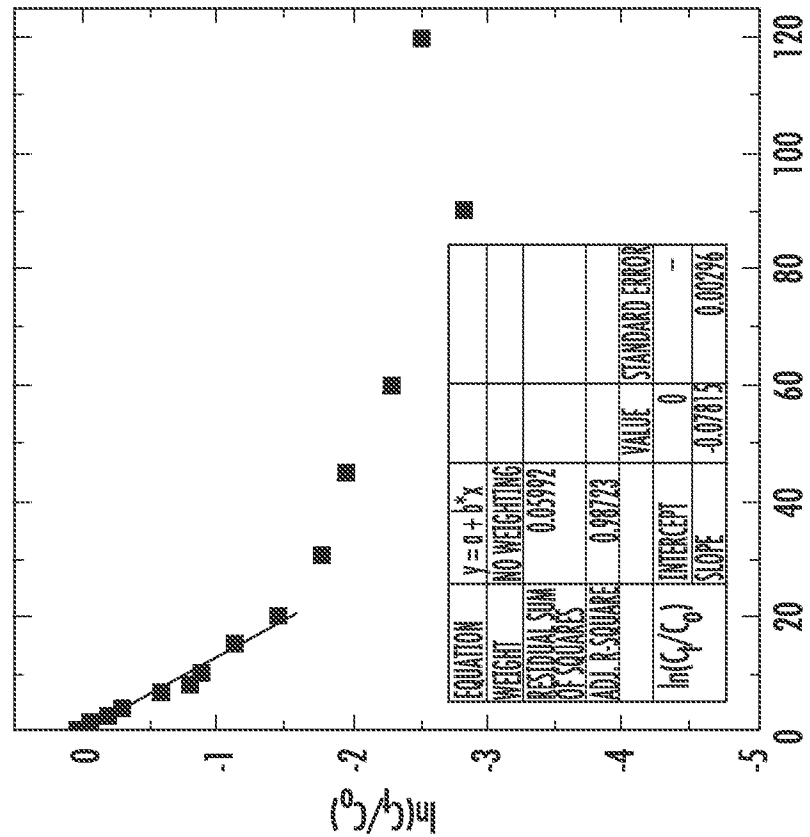


FIG. 72D

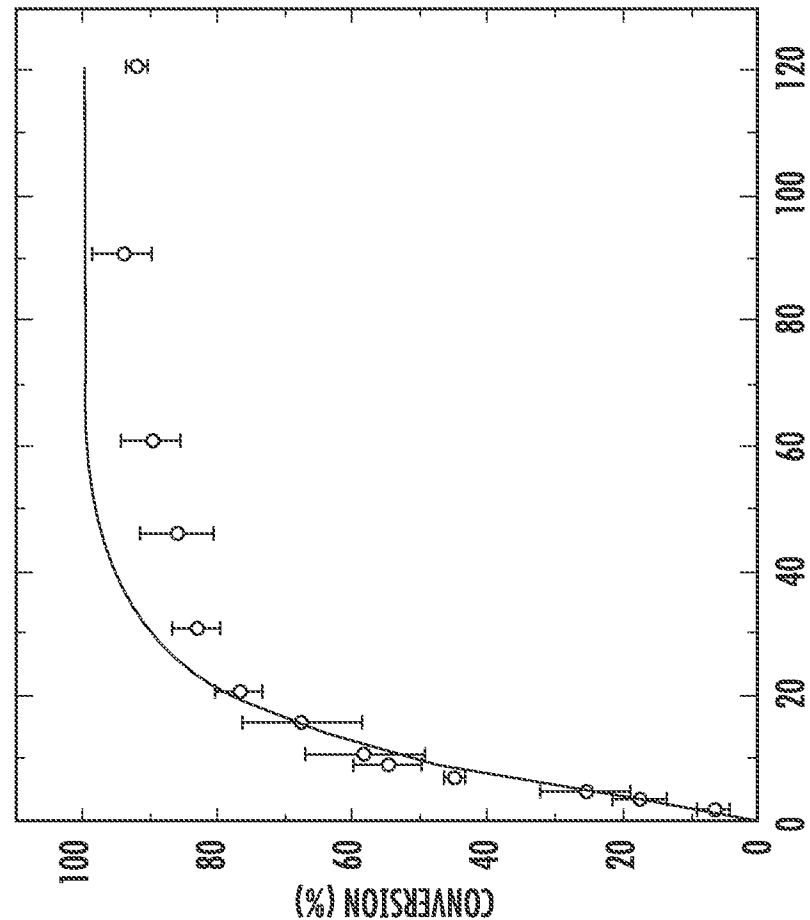
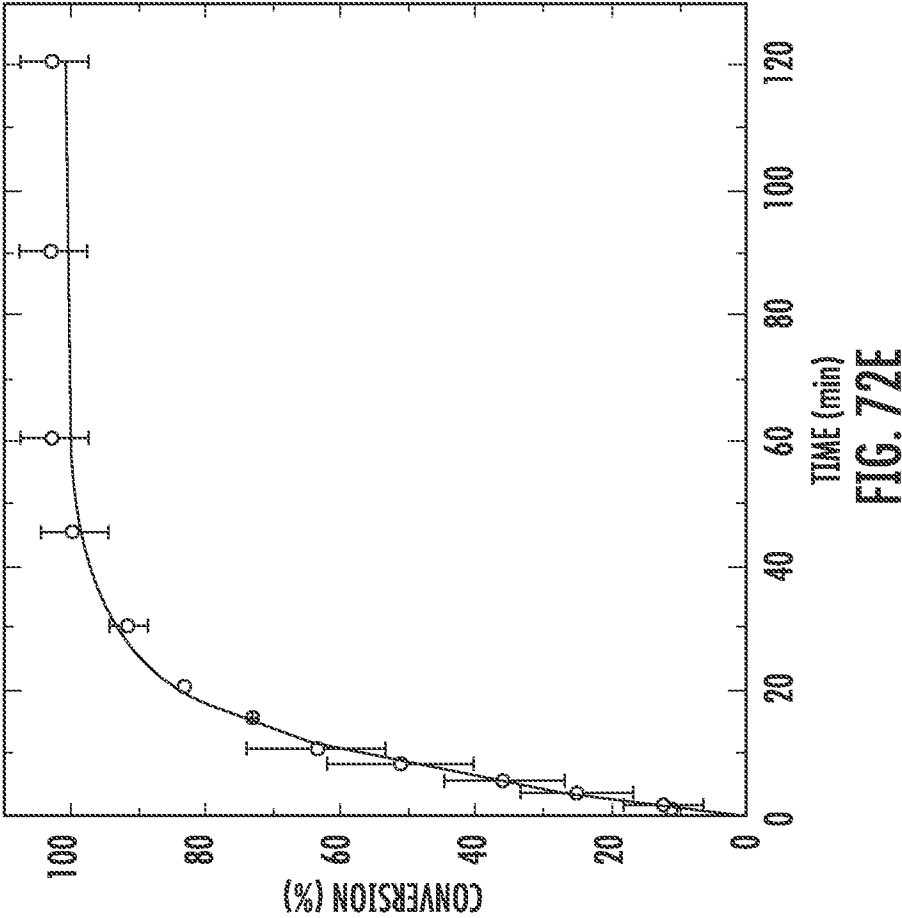
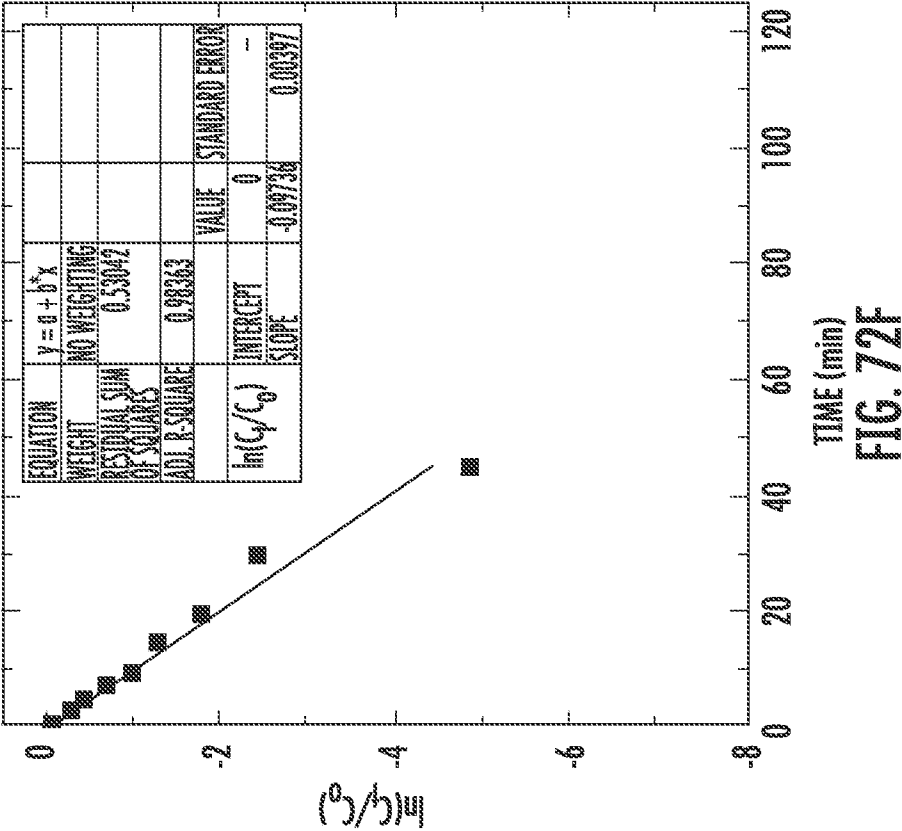


FIG. 72C



39/45

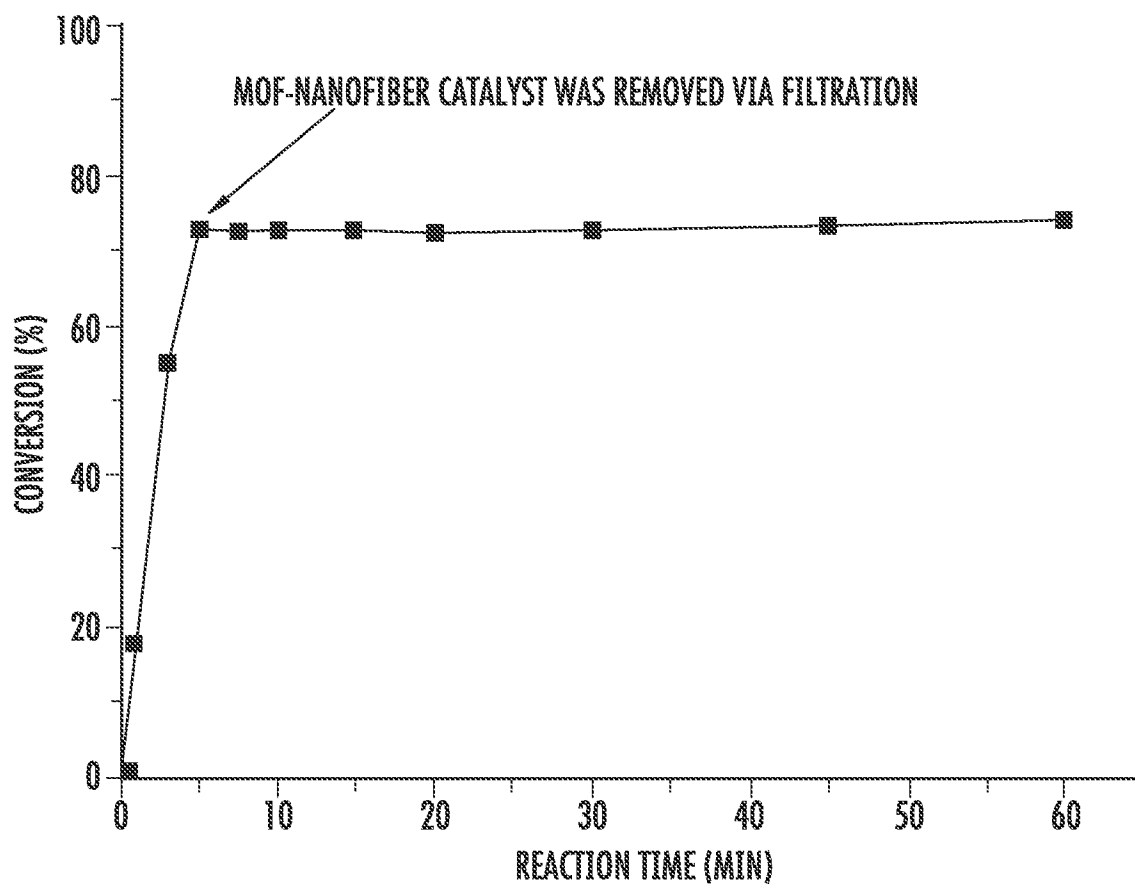


FIG. 73

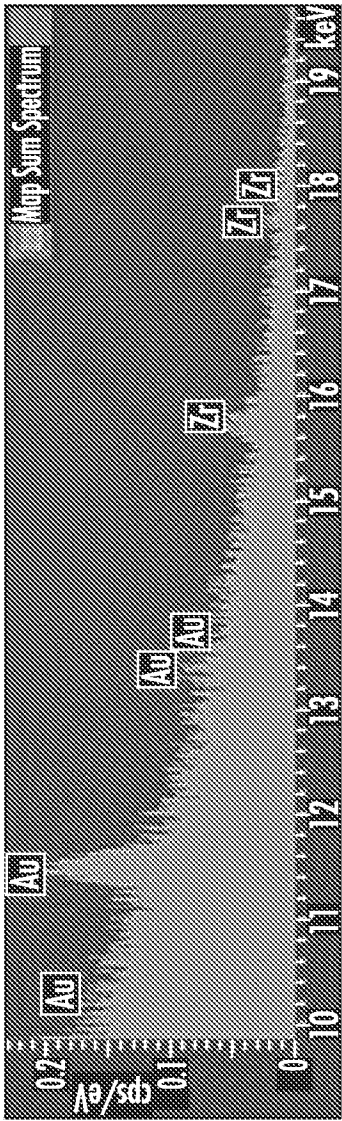


FIG. 74B

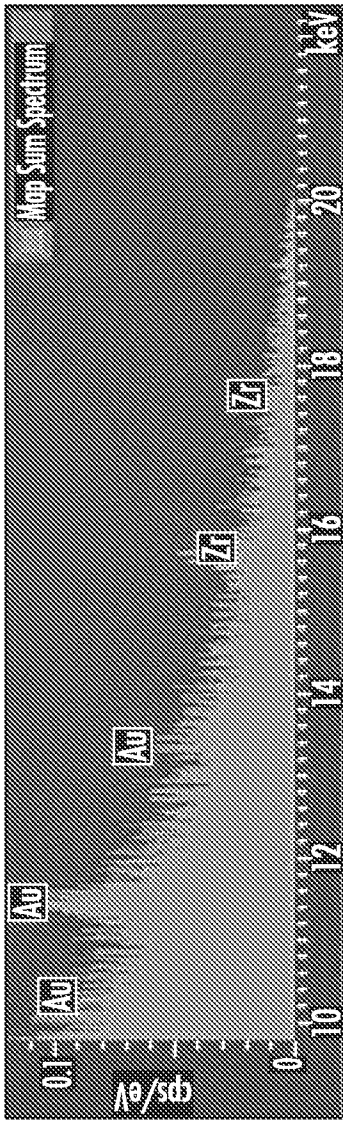


FIG. 74D

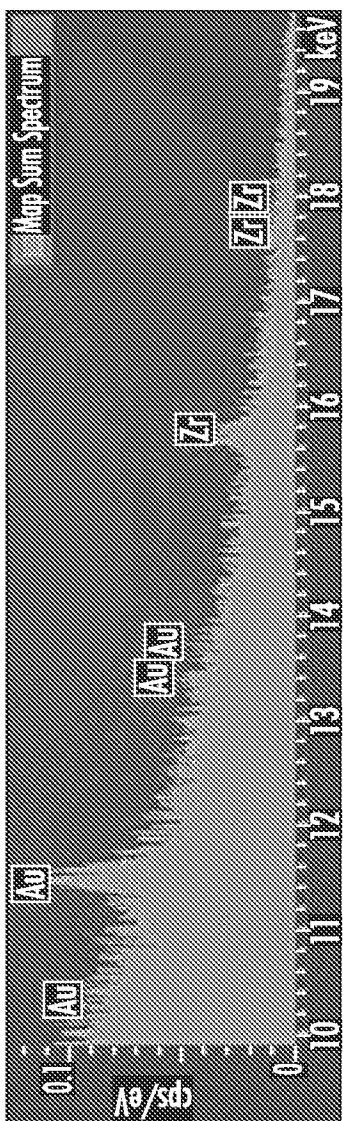


FIG. 74F

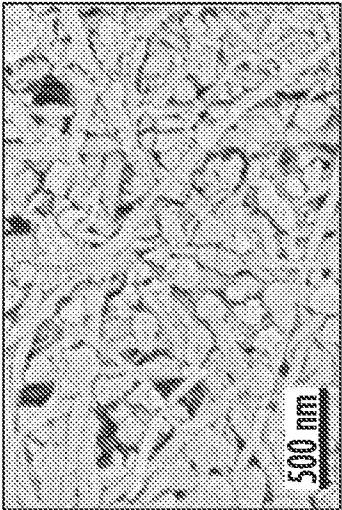


FIG. 74A

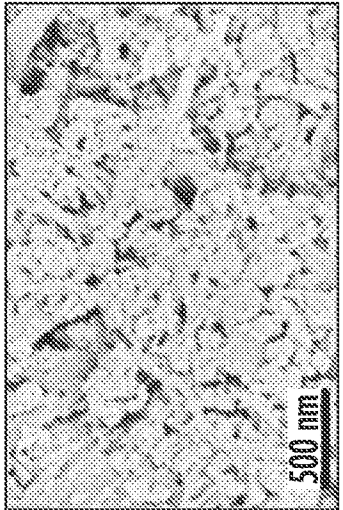


FIG. 74C

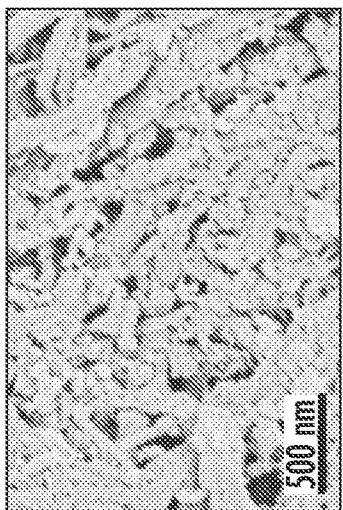


FIG. 74E

41/45

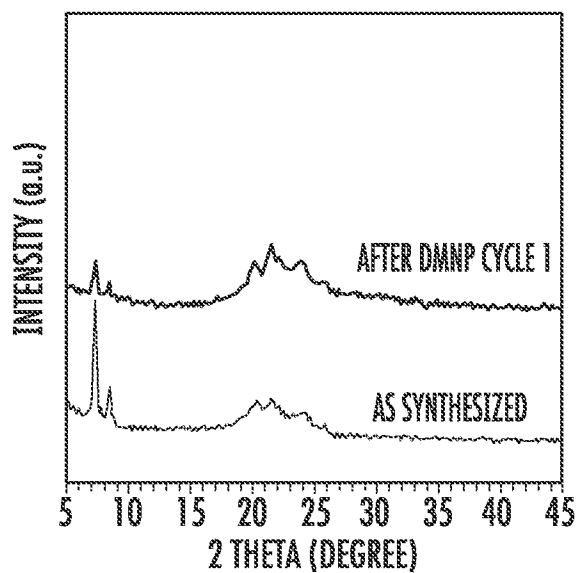


FIG. 75A

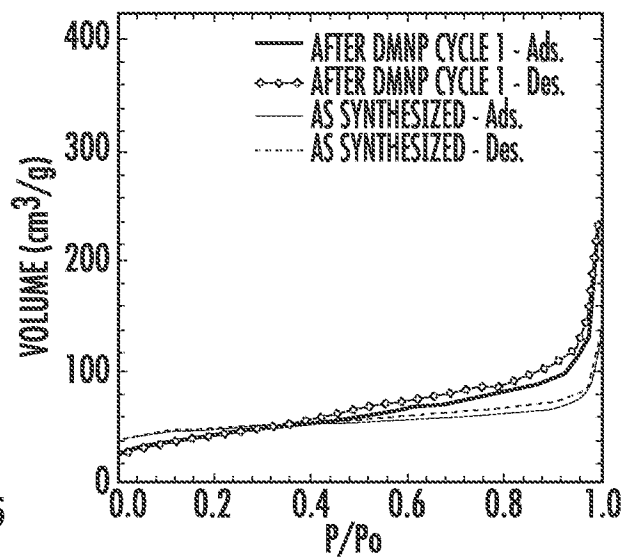


FIG. 75B

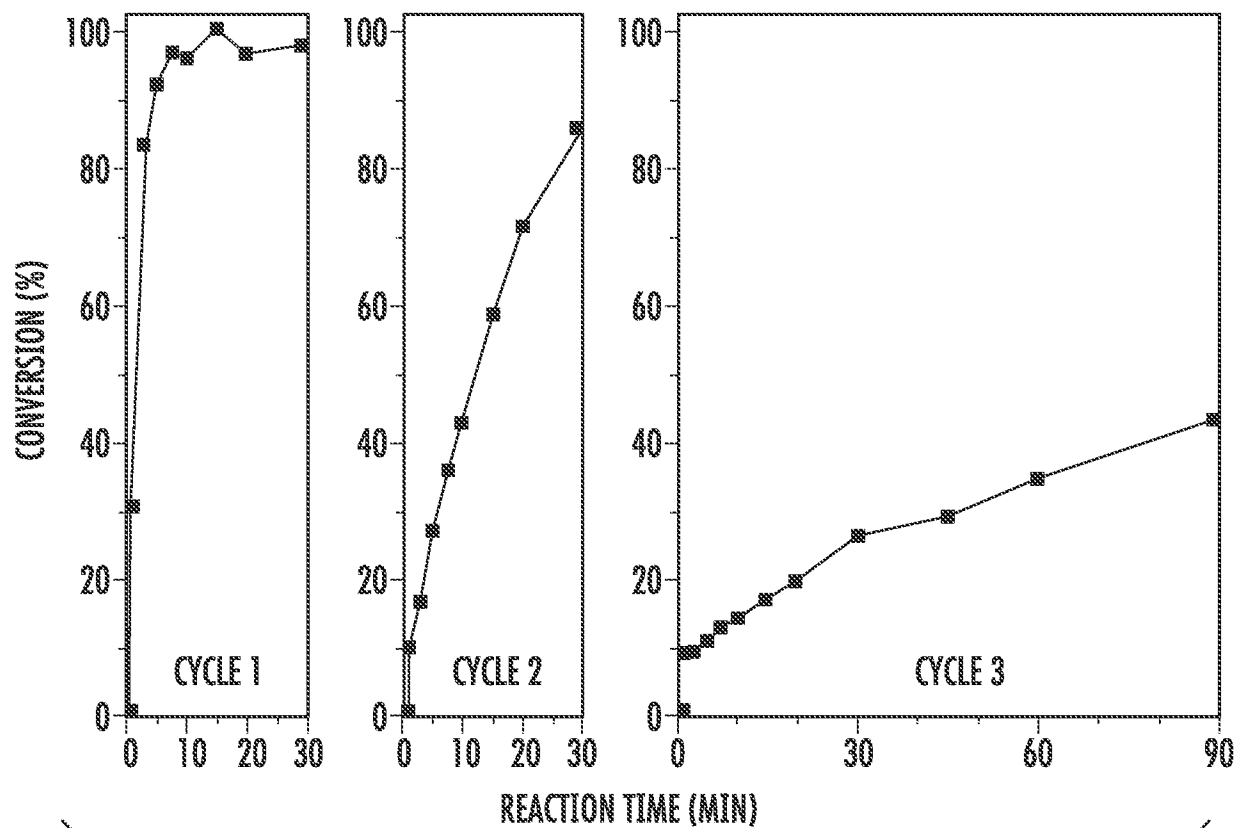
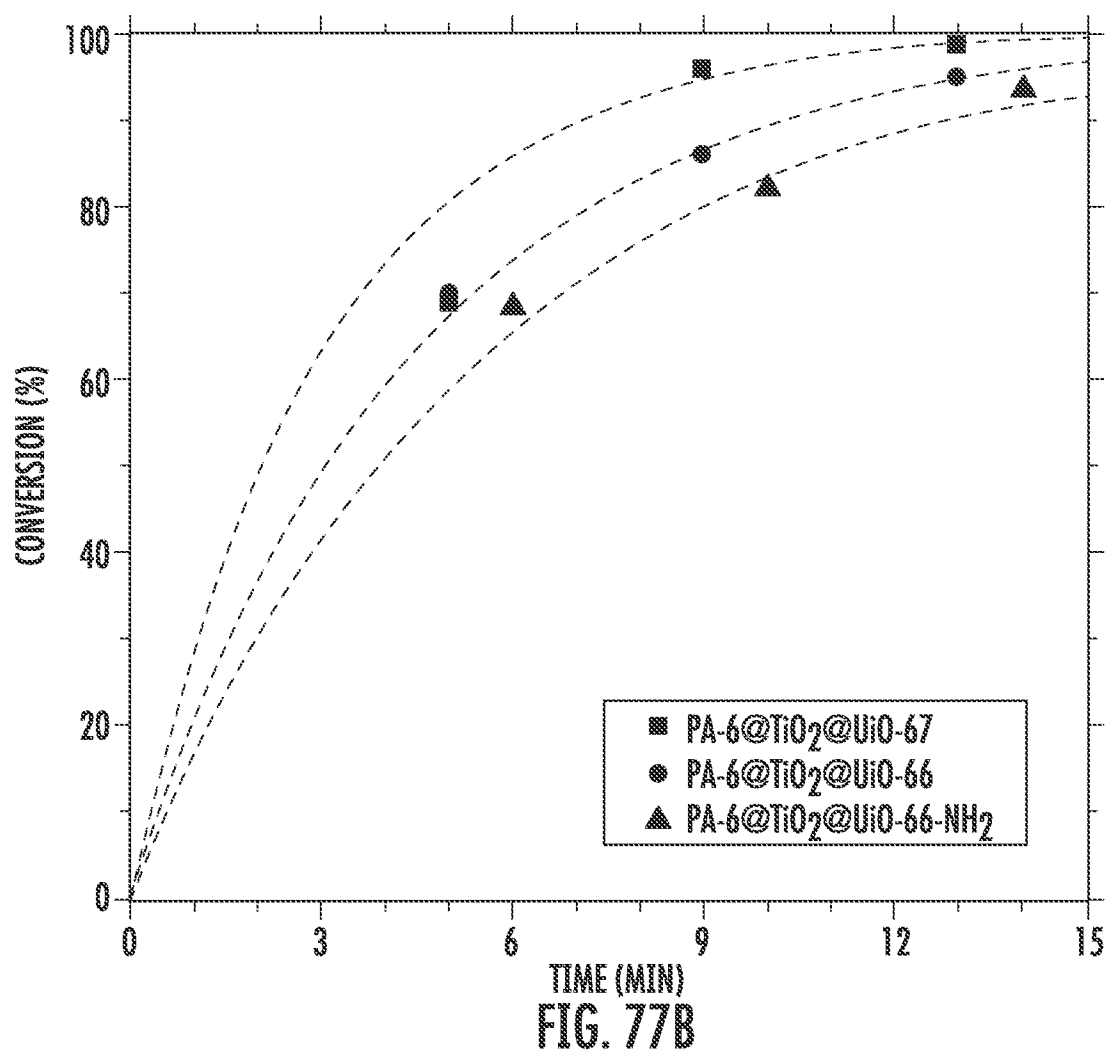
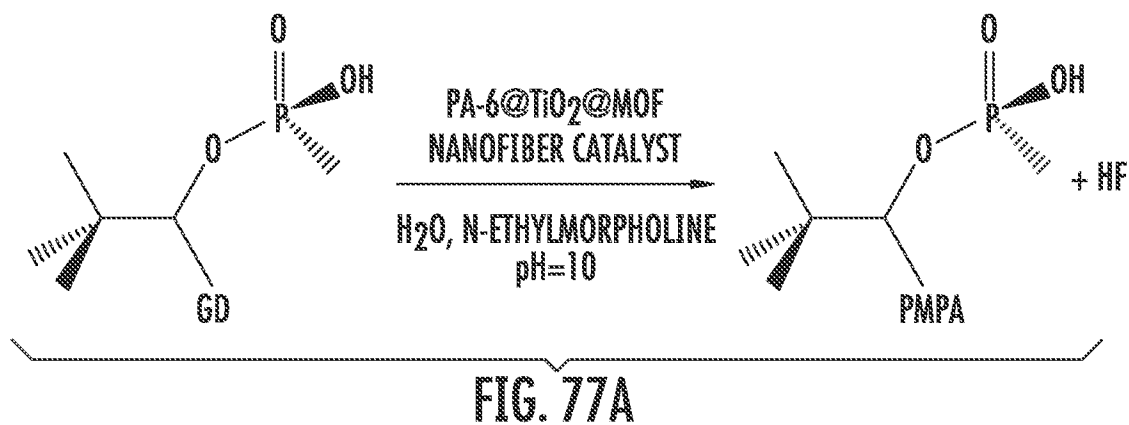
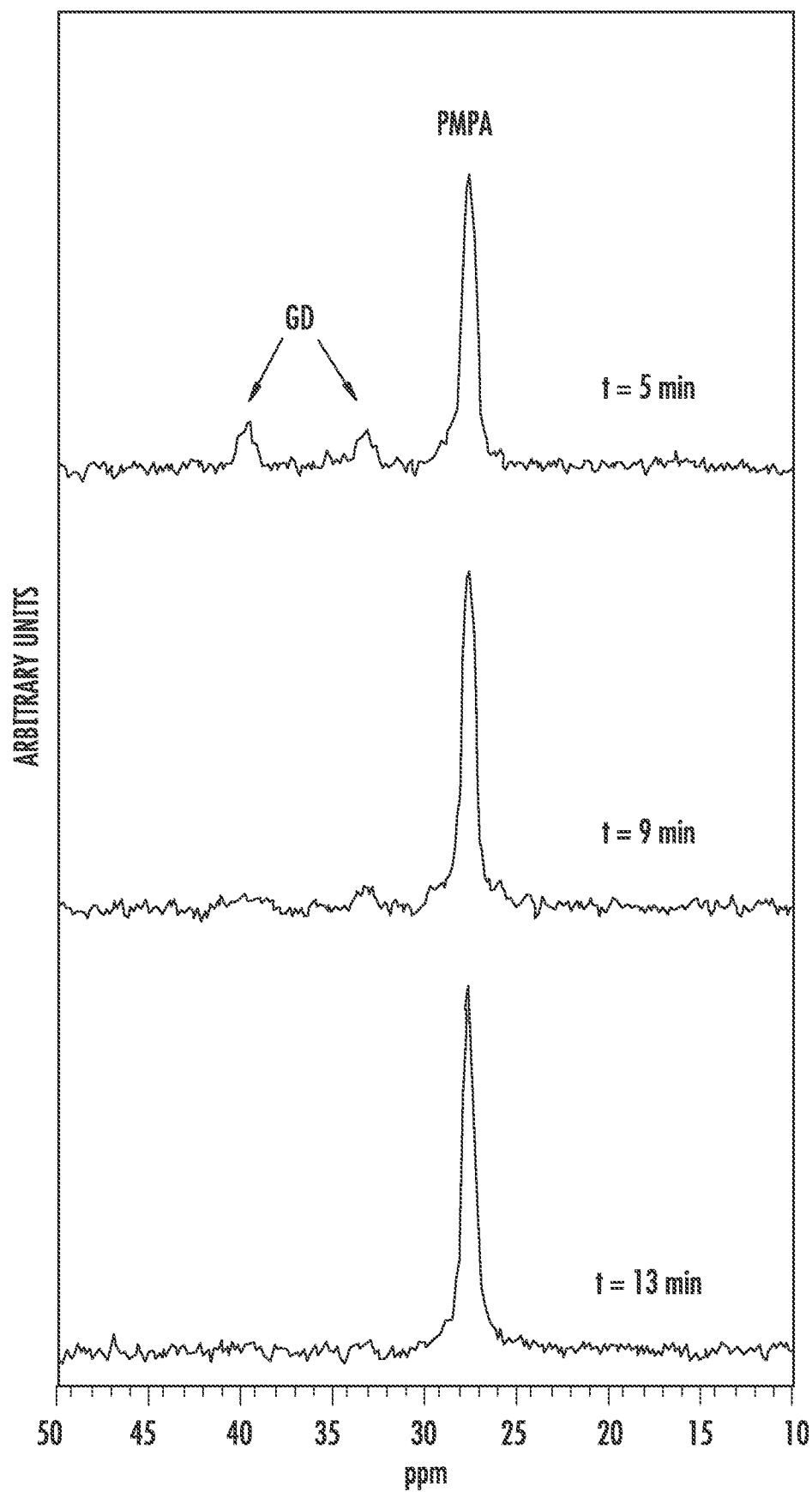


FIG. 76

42/45



43/45

**FIG. 78**

44/45

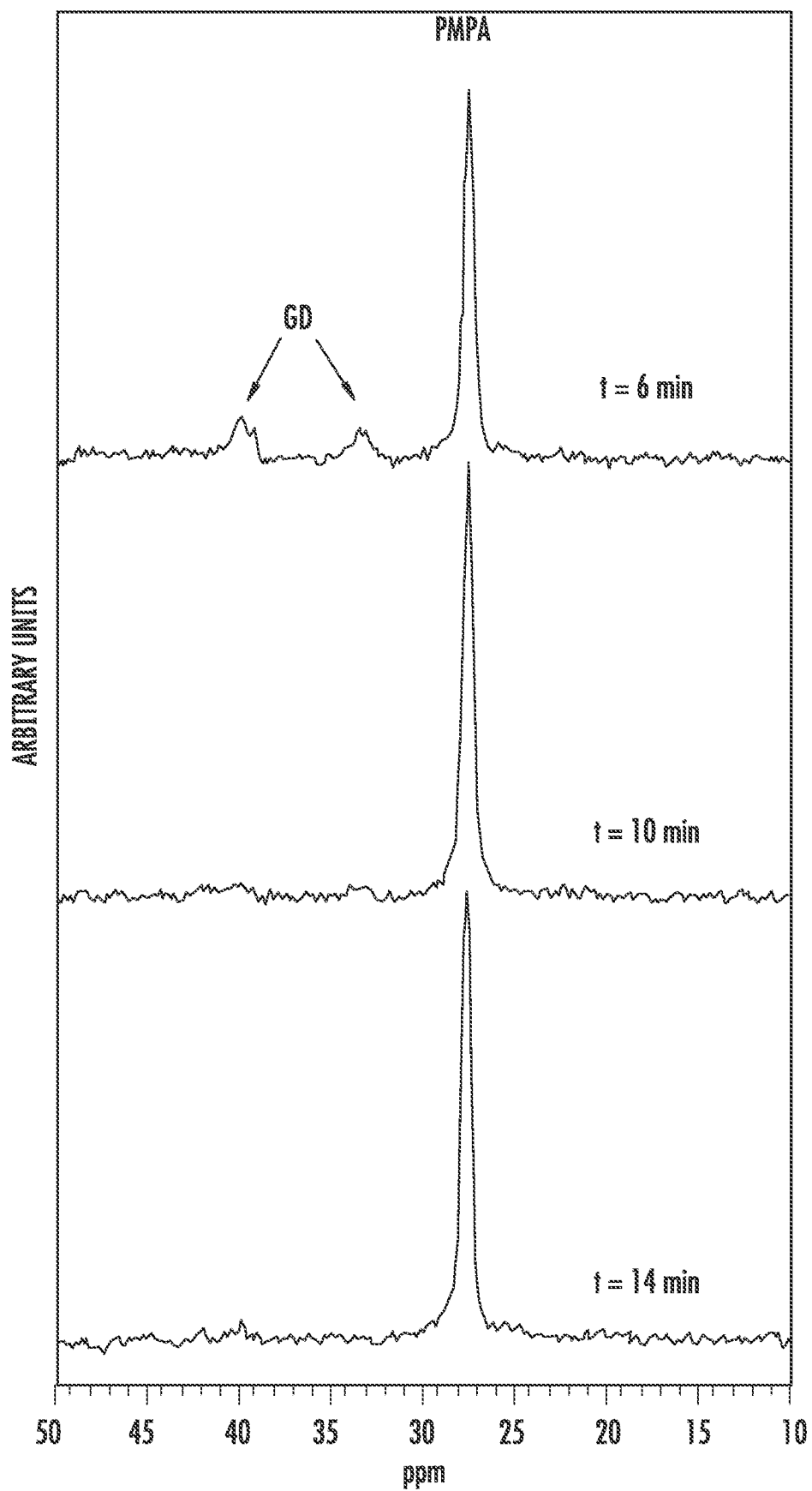


FIG. 79

45/45

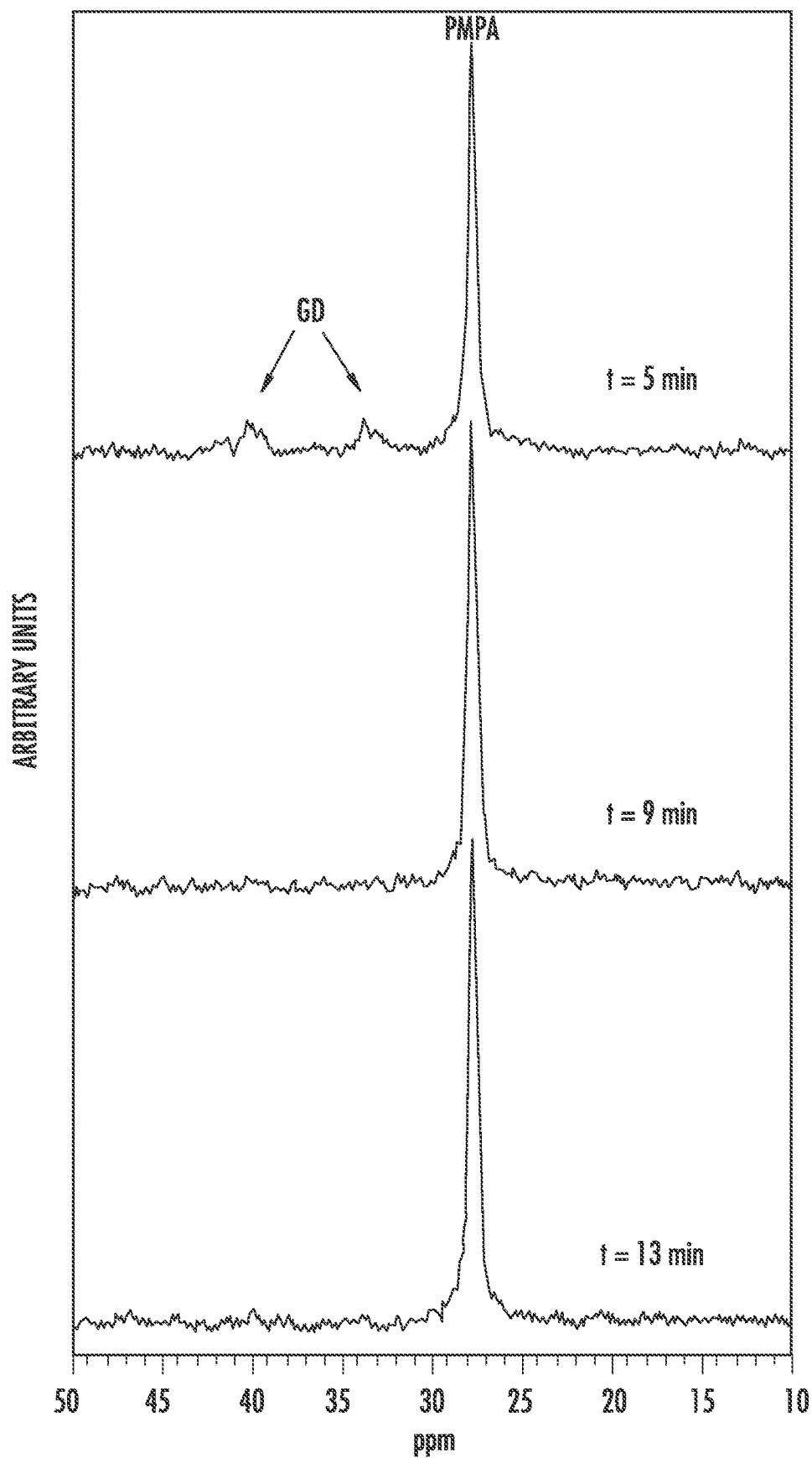


FIG. 80

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 17/38266

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01J 20/28, B01J 20/32, B01J 20/22, B01D 15/00 (2017.01)

CPC - B01D 2257/406, B01J 20/3217, B01J 20/28033, B01D 15/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

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

See Search History Document

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

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZHAO et al, 'Facile Conversion of Hydroxy Double Salts to Metal-Organic Frameworks Using Metal Oxide Particles and Atomic Layer Deposition Thin-Film Templates', Journal of the American Chemical Society, volume 137, 11 October 2015 (11.10.2015), pg 13756-13759 and associated Supporting Information	1-4
X — Y	ALAVI et al, 'Synthesis and characterization of different nanostructured copper(II) metal-organic frameworks by a ligand functionalization and modulation method', CrystEngComm, volume 16, 6 January 2014 (06.01.2014), pg 2246-2250.	64 — 65-67
Y	RODENAS et al, 'Metal-organic framework nanosheets in polymer composite materials for gas separation', Nature Materials, volume 14, 2 November 2014 (02.11.2014), pg 48-55 and associated Supplementary Information.	65-67
A	ZHAO et al, 'Enhancing Gas Adsorption and Separation Capacity through Ligand Functionalization of Microporous Metal-Organic Framework Structures', Chemistry - A European Journal, volume 17, issue 18, 23 March 2011 (23.03.2011), pg 5101-5109.	65-67
A	CARSON et al, 'Structure Solution from Powder Diffraction of Copper 1,4-Benzenedicarboxylate', European Journal of Inorganic Chemistry, volume 2014, issue 12, 13 March 2014 (13.03.2014), pg 2140-2145.	65-67
X	LEMAIRE et al, 'Copper Benzenetricarboxylate Metal-Organic Framework Nucleation Mechanisms on Metal Oxide Powders and Thin Films formed by Atomic Layer Deposition', ACS Applied Materials and Interfaces, volume 8, issue 14, 21 March 2016 (21.03.2016), pg 9514-9522.	1-4



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search
12 October 2017

Date of mailing of the international search report

13 NOV 2017

Name and mailing address of the ISA/US
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Authorized officer:
Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 17/38266

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-63, 68-92
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

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

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 17/38266

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X —	YU et al, 'Precisely tailoring ZIF-67 nanostructures from cobalt carbonate hydroxide nanowire arrays: toward high-performance battery-type electrodes'. Journal of Materials Chemistry A: Materials for Energy and Sustainability, volume 3, issue 32, 8 July 2015 (08.04.2015), pg 16688-16694.	1-4
X —	MAJANO et al, 'Room-temperature synthesis of Fe - BTC from layered iron hydroxides: the influence of precursor organization', CrystEngComm, volume 15, 9 August 2013 (09.08.2013), pg 9885-9892.	1-4
X — A	SHEKHAH et al, 'Post-synthetic modification of epitaxially grown, highly oriented functionalized MOF thin films', Chemical Communications, volume 40, issue 47, 19 September 2011 (19.09.2011), pg 11210-11212.	64 — 65-67
X — A	LIU et al, 'Multi Variant Surface Mounted Metal-Organic Frameworks', Advanced Functional Materials, volume 23, 1 March 2013 (01.03.2013), pg 3790-3798.	64 — 65-67
X — A	MEILIKHOV et al, 'Binary Janus Porous Coordination Polymer Coatings for Sensor Devices with Tunable Analyte Affinity, Angewandte Chemie International Edition, volume 52, issue 1, 4 November 2012 (04.11.2012), pg 341-345.	64 — 65-67