



(51) International Patent Classification:

B01D 53/26 (2006.01) B01J 20/02 (2006.01)
B01J 20/32 (2006.01) B01D 15/08 (2006.01)

(21) International Application Number:

PCT/US2024/013243

(22) International Filing Date:

26 January 2024 (26.01.2024)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/483,968 08 February 2023 (08.02.2023) US

(71) Applicant: **THE REGENTS OF THE UNIVERSITY OF CALIFORNIA** [US/US]; 1111 Franklin Street, 12th Floor, Oakland, California 94607 (US).

(72) Inventors: **YAGHI, Omar M.**; 2150 Shattuck Ave., Suite 510, Berkeley, California 94704 (US). **SONG, Woochul**; 2150 Shattuck Ave., Suite 510, Berkeley, California 94704 (US).

(74) Agent: **OSMAN, Richard**; 530 Lawrence Expy #332, Sunnyvale, 94085 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY,

MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

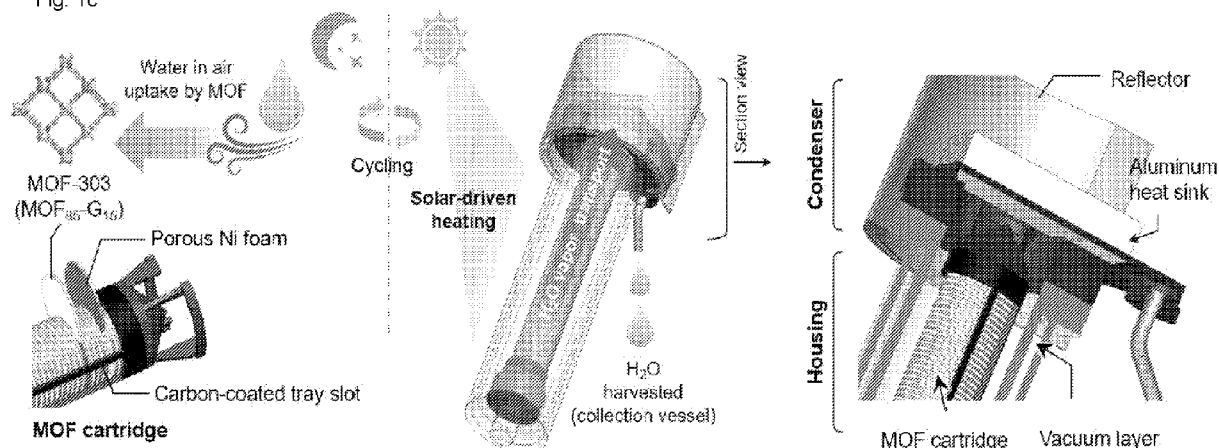
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR,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

Published:

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

(54) Title: SCALABLE AND PASSIVE MOF ASSISTED ATMOSPHERIC WATER HARVESTER

Fig. 1c



(57) Abstract: A scalable and passive sorbent assisted atmospheric water harvester that uses the sorbent to transform water in air into drinkable water, only using natural sunlight and ambient temperatures.

Scalable and Passive MOF Assisted Atmospheric Water Harvester

This invention was made with government support under HR0011-21-C-0020 awarded by the DOD Advanced Research Projects Agency. The government has certain rights in the invention.

[001] Introduction

[002] Although access to water is recognized as a fundamental human right, over five billion people are expected to experience water stress by the year 2050¹⁻³. Climate change is exacerbating this problem by causing severe droughts and therefore affecting the lives and livelihoods of large segments of the world population^{4,5}. Water desalination offers a solution but this process and the transport of water where it is needed are energy intensive. Given that there is almost as much water in the atmosphere at any given time as there is in lakes and rivers on our planet, the question of whether this water could be harvested in an energy efficient manner is foundational to solving the water scarcity problem⁶⁻⁸. Herein, we report the design and construction of a device into which a metal-organic framework (MOF) material has been integrated in a form to maximally expose it to air and allow the extraction of water at night and its collection during the day when exposed to ambient sunlight. This MOF water harvester was demonstrated in the Death Valley desert air in the month of August 2022 demonstrating the ability to collect 114 to 210 g·H₂O/kg·MOF/day under ambient temperature swing of 30 to 60 °C between night and day with a relative humidity (RH) ranging from 7 to 21%. No other water harvesting system has been reported to operate under such extreme conditions and without energy input aside from ambient sunlight.

[003] Others and we have developed atmospheric water harvesting (AWH) based on MOFs⁹⁻¹¹, porous polymers¹², zeolites¹³, and other porous or hygroscopic materials¹⁴⁻¹⁷. Harvesters based on these have been tested either in the laboratory^{11,17}, the field, or both^{9,10,12-16} with power supply (i.e. active). Only one system using ambient sunlight with no other source of energy or power (i.e. passive) has been tested in the desert (**Fig. 1a**)¹⁸. Our current MOF water harvester collected double the amount of water per kilogram of MOF (g·H₂O/kg·MOF) under even more extreme conditions in the Death Valley (**Fig. 1b**). In particular, the device was loaded with MOF-303 [Al(OH)(PZDC); PZDC, 1*H*-pyrazole-3,5-dicarboxylate], of which water isotherm has the water uptake inflection point at 12% RH with uptake capacity of 39 wt% at 20% RH^{9,18-20}.

[004] This new generation MOF water harvesters reported here was developed focusing on the following criteria: (1) increasing the volume-to-surface area ratio (VS-r) of MOF bed, (2)

designing MOF bed assembly (MOF cartridge) to efficiently distribute heat under the solar irradiance, and (3) optimizing the condenser to accelerate the condensation rates. Each step is responsible for effective water sorption, desorption, and condensation that are critical for AWH. In addition, the MOF cartridge was designed to have constant VS-r irrespective of the MOF amounts used in the device; an aspect that improve its scalability. As a result of these factors, the present harvester enabled completely passive AWH even under the extremely dry and hot air conditions in the Death Valley where the highest ambient temperature near the ground was 60 °C and the lowest average-RH (RH_{avg}) of the nights was 14% during our field tests.

[005] Summary of the Invention

[006] The invention provides methods and compositions for scalable and passive sorbent assisted atmospheric water harvesting.

[007] In an aspect, the invention provides a scalable and passive sorbent assisted atmospheric water harvester device that uses the sorbent to transform water in air into drinkable water, only using natural sunlight and ambient temperatures.

[008] In embodiments:

[009] the sorbent is selected from a metal-organic framework (MOF), which maybe aluminum-based, such as MOF-303, a covalent organic framework (COF), which may be boron or nitrogen-based, and a zeolite.

[010] comprising optimization processes of water sorption, desorption and condensation processes at device scale to improve water harvesting capacity.

[011] configured to provide drinking, agricultural, and municipal water, or for sorption-driven heat exchangers, humidity control for many industrial processes, heat pumps, etc.

[012] configured to provide up-scalable MOF-assisted passive AWH to (1) increase the ratio of volume-to-surface area of MOF bed (SV-r), (2) design MOF bed assembly (MOF cartridge) to efficiently use natural sunlight, and/or (3) optimize the condenser to accelerate water condensation properties, wherein each feature preferably contributes synergistically to effective water sorption, desorption, and condensation for AWH at practical scale.

[013] configured to improving the scalability of the device, wherein the MOF cartridge is designed and configured to have the constant SV-r irrespective of MOF amounts integrated into the device; for example, in particular embodiments, this device can produce water up to ~285 g•H₂O/kg•MOF-303/day.

[014] configured essentially as described in this application, and/or as shown in the Figures herein.

[015] configured to comprise two compartments: one is the housing for the MOF bed cartridge and the other is the condenser, wherein the cylinder-shape housing has a vacuum insulated double-wall structure to prevent conductive heat loss to the environment, wherein the projected area of the cylinder body toward the solar irradiation is consistent alongside the sun trajectory, maximizing the use of solar energy from the sun rise to the sun set; wherein the condensation compartment is located on top of the housing to promote water condensation as well as vapor transport from the housing to condenser by air density (temperature) differences; wherein the MOF cartridge and condenser may require different thermal conditions to improve AWH during the day cycle; wherein the condenser may face clear sky, to use radiative energy dissipation to accelerate water condensation rates in the future.

[016] configured to comprise a MOF bed assembly (cartridge) is designed to maintain the SV-r as 2.6, irrespective of the amounts of MOFs used in the device, for example wherein MOF powders were pressed into the thin disc pellets with 38 mm in diameter and ~0.8 mm in height, and these pellets are stacked with porous nickel (Ni) foam discs (38 mm in diameter and 1.5 mm in height). As the porosity of the Ni foam is higher than 97%, the external air can flow or diffuse through this porous media, making the inter-facing MOF pellet surfaces exposed to the air. Also, Ni foam has the $\sim 90 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ thermal conductivity and can serve as heat conductor in between MOF pellets under the solar irradiation, which is also important for efficient water desorption as the MOFs are nonconductive.

[017] configured to comprise a patterned surface coating of the condenser, such as a line-patterned hydrophobic (carbon nanofiber and polytetrafluoroethylene blends, CNF/PTFE) surface coating¹¹ of the condenser to improve the water productivity. In embodiments, the pattern has the same direction with gravity, to promote initial water nucleation and grow coalesced water droplets in the hydrophilic channels, and then remove condensed water by gravity rather than let water adhered over the entire metal contact due to the high surface energy. By this modification, water harvesting capacity increased from $\sim 160 \text{ g} \cdot \text{H}_2\text{O} / \text{kg} \cdot \text{MOF-303} / \text{day}$ (non-coated aluminum condenser) to $250 \text{ g} \cdot \text{H}_2\text{O} / \text{kg} \cdot \text{MOF-303} / \text{day}$.

[018] configured to comprise environmentally-friendly actuators, so that the transition of the device's operational modes between water sorption (night cycle) and desorption (day cycle) can be carried out automatically, such as configured with solar panels and/or small batteries with minimum electrical components, and preferably configured to produce water with near zero carbon emission, wherein actuation is performed without any electricity, including embodiments deploying thermal actuators like wax motors that are operated only by ambient temperature gradients during the day and night.

[019] In an aspect, the invention provides a method of harvesting water comprising operating a device herein to capture and collect water from air.

[020] The invention encompasses all combinations of the particular embodiments recited herein, as if each combination had been laboriously recited.

[021] Brief Description of the Drawings

[022] **Figs. 1a-d.** New generation of passive MOF water harvester. (a) Operational conditions of representative MOF^{9,10,18} and zeolite¹³ based water harvesters tested in the field. Only one passive water harvester was tested in the field (Arizona, AZ, desert). RH_{ads} (%): RH during sorption cycle. T_{des} (°C): average ambient temperature during desorption cycle. (b) AWH capacity per one harvesting cycle. For refs 9 and 10, average values during the day and the night were used. For this work, average value of five field test results in both Berkeley and the Death Valley is used. (c) General configuration of the MOF water harvester. At night, MOF cartridge is exposed to air to capture atmospheric water. During the day, the MOF cartridge is assembled into the vacuum-insulated device housing and condenser. Upon the solar irradiance, water is released from MOF by solar-driven heating and transported to the condenser. Direct solar irradiance to the condenser is shielded by reflector, and water is condensed at the surface of aluminum heat sinks. Condensed water is collected into the collection vessel connected to the condenser by the tube. (d) Schematic illustration showing the projected area differences (red lines) between cylindrical and rectangular shape bodies from sunrise to sunset.

[023] **Figs. 2a-d.** MOF cartridge design and water uptake properties. (a) Photographs of the MOF cartridge, MOF₈₅-G₁₅ pellet and porous Ni foam disc. (b) N₂ isotherm of MOF-303 and MOF₈₅-G₁₅ pellet at 77 K. (c) Water isotherm of MOF-303 and MOF₈₅-G₁₅ pellet at 25 °C. (d) Weight change of the MOF cartridge at 25 °C and 40% RH. The weight change is presented normalized to the MOF-303 weight (35 g). Error bars are the standard deviation of three independent measurements.

[024] **Figs. 3a-e.** Laboratory test of the passive AWH device. (a) Simulated and experimental temperature change of the MOF cartridge and condenser under light irradiance. (b) Experimental RH change of the MOF housing and condenser during the laboratory test. (c) AWH capacity of the device tested with different surface conditions of the condensers, which are bare aluminum (Al, non-treated), PTFE coated, CNF/PTFE coated, and patterned coating with CNF/PTFE. (d) Water-air interface contact angle measurements of bare (Al), PTFE- and CNF/PTFE-coated condensers. (e) Photograph of the condenser surface with linear patterned CNF/PTFE coating (black strips) alongside the direction of gravity.

[025] **Figs. 4a-d.** AWH in Berkeley. (a) Photographs of the device setup including power station (500 Wh), pyranometer and data acquisition (DAQ) systems, and water collected at different time during the Jun-10 test. (b) Sectional drawing of the device to show the different measurement points of temperature and RH. Sectional plane caps are colored with turquoise for visual clarity. (c) Temperature ($^{\circ}\text{C}$), solar irradiance (W/m^2), and RH (%) changes of the device and ambient air conditions during the Jun-10 test. Time axes are synced with each other. (d) Comparison of AWH capacity between the lab and Berkeley field test conditions.

[026] **Figs. 5a-d.** AWH in the Death Valley. (a) Photographs of the AWH at Furnace Creek, showing the MOF cartridge exposed to air for water uptake (upper left), the device during the day cycle (upper right), and water collected at different time (bottom). (b) Temperature ($^{\circ}\text{C}$), solar irradiance (W/m^2), and RH (%) changes of the device and ambient air conditions during the Aug-23 test. Time axes are synced with each other. (c and d) AWH capacity as a function of RH_{avg} (c) and T_{avg} (d) during the night and day cycles, respectively.

[027] **Fig. 6.** 3D Drawings of the device structure with different views.

[028] **Fig. 7.** 3D Drawings of the expanded device structures to show the assembly (and disassembly) of the MOF cartridge with the MOF housing and condenser components, between the night and day AWH cycles.

[029] **Fig. 8.** Sectional view of the device to illustrate the direction of vapor and liquid water transport during the day cycles of AWH. Sectioned planes are capped with turquoise color for visual clarity.

[030] **Figs. 9a-b.** (a) Drawings of the MOF housing part with the dimensions. The unit is millimeter (mm). (b) Photographs of the MOF housing part, showing the 1/8 FNPT threaded vacuum port and the valve connected to the outer shell of the housing. Vacuum port is not shown in the drawing models.

[031] **Fig. 10.** Drawings of the MOF cartridge with the dimensions. The unit is millimeter (mm).

[032] **Figs. 11a-c.** Drawings of the (a) condenser housing and (b) aluminum heat sink parts with the dimensions. The unit is millimeter (mm). (c) Schematic illustration of assembling condenser housing and two heat sinks. Epoxy glue was applied to make leak-tight seals between the parts.

[033] **Fig. 12.** Drawings of the light reflector part the dimensions. The unit is millimeters (mm).

[034] **Fig. 13.** Side-by-side comparison of the device modeling (left panel) and the entire device set-up including the measurement devices (right panel).

[035] **Fig. 14.** PXRD spectra of activated MOF-303 and graphite powder, sorbent pellets prepared using MOF-303 without graphite (MOF₁₀₀), 95 wt% MOF-303 and 5 wt% graphite (MOF₉₅-G₅), 90 wt% MOF-303 and 10 wt% graphite (MOF₉₀-G₁₀), and 85 wt% MOF-303 and 15 wt% graphite (MOF₈₅-G₁₅), respectively.

[036] **Fig. 15.** N₂ isotherm (at 77 K) of the sorbent pellets prepared using MOF-303 without graphite binders. BET surface area is 1200 m²/g.

[037] **Fig. 16.** N₂ isotherm (at 77 K) of the sorbent pellets prepared using 95 wt% MOF-303 and 5 wt% graphite binders. BET surface area is 1080 m²/g pellet (1130 m²/g MOF-303).

[038] **Fig. 17.** N₂ isotherm (at 77 K) of the sorbent pellets prepared using 90 wt% MOF-303 and 10 wt% graphite binders. BET surface area is 1130 m²/g (1255 m²/g MOF-303).

[039] **Fig. 18.** FT-IR spectra of activated MOF-303 powder, sorbent pellets prepared using MOF-303 without graphite (MOF₁₀₀) and 85 wt% MOF-303 and 15 wt% graphite binders (MOF₈₅-G₁₅), respectively.

[040] **Fig. 19.** Photographs of the fractured sorbent pellet pieces in water for 24 hours. The sorbent pellets were prepared using 85 wt% MOF-303 and 15 wt% graphite binders (MOF₈₅-G₁₅), and 85 wt% MOF-303 and 15 wt% cellulose binders (MOF₈₅-C₁₅), respectively.

[041] **Figs. 20a-c.** Water uptake of MOF cartridge. Time-dependent weight change of the MOF cartridge at 25 °C and 40 % RH with the MOF-303 amounts of (a) 25 g, (b) 35 g and (c) 45 g, respectively. Error bars are the standard deviation of three independent measurements.

[042] **Fig. 21.** Energy and heat transfer simulation of the device under the solar irradiance. (a) Time-dependent temperature plots of the device simulated for 7 hours (420 min). The direction of the external irradiation was set as (-1, 0, -1) during the course of simulation.

[043] **Figs. 22a-d.** Lab tests of the device using different condensers. Representative plots of temperature (°C, left panel) and RH (% , right panel) changes of the device using the condensers with (a) non-, (b) PTFE-, (c) CNF/PTFE-, and (d) pattern-coated surfaces.

[044] **Fig. 23.** Temperature (°C), solar irradiance (W/m²), and RH (%) changes of the device and ambient air conditions during the Jun-2 test in Berkeley. Time axes are synced with each other.

[045] **Figs. 24a-d.** Photographs of the device test in the Death Valley area (36.5319° N, - 116.5455° W). (a) Device, data acquisition system (DAQ), and laptop without cable connection. (b) Photograph taken during the day cycle of the August 20 test with cable connections. Parasol was used to protect the electrical devices from the direct exposure to sunlight. (c) MOF cartridge during the night cycle. (d) Device after the day cycle test is completed.

[046] **Figs. 25a-b.** Photographs of the device test in the Furnace Creek (36.4506 ° N, - 116.8523° W). (a) MOF cartridge during the night cycle of the August 23 2022 test. (b) Device

at the end of the day cycle (after sun set). Red cargo box was used to protect the electrical devices from the direct exposure to sunlight.

[047] **Fig. 26.** Temperature ($^{\circ}\text{C}$), solar irradiance (W/m^2), and RH (%) changes of the device and ambient air conditions during the August 20 test. Time axes are synced with each other. Recording of solar irradiance data was terminated at ~7 AM due to the malfunction of the measurement device.

[048] **Fig. 27.** Temperature ($^{\circ}\text{C}$), solar irradiance (W/m^2), and RH (%) changes of the device and ambient air conditions during the August 21 test. Time axes are synced with each other.

[049] **Figs. 28a-b.** (a) Device design variation that has moving parts operated by thermal actuator. (b) Actuation mechanism of wax motor and device configurations in each mode: embodiments that uses thermal actuator (wax motor) to change the operational modes automatically between the day and night cycles, only using the ambient temperature gradients without any electricity.

[050] **Description of Particular Embodiments of the Invention**

[051] Unless contraindicated or noted otherwise, in these descriptions and throughout this specification, the terms “a” and “an” mean one or more, the term “or” means and/or. It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application and scope of the appended claims. All publications, patents, and patent applications cited herein, including citations therein, are hereby incorporated by reference in their entirety for all purposes.

[052] **General structure of the passive AWH device.** The device is designed to have two main compartments. One is the housing for the MOF bed cartridge and the other is the condenser. The cylinder-shape housing has a vacuum insulated double-wall structure to prevent conductive heat loss to the environment. Also, compared to the rectangular geometry that other passive devices generally adopted, the projected area of the cylinder body toward the solar irradiation is consistent alongside the sun trajectory, maximizing the use of solar energy from the sun rise to the sun set. The condensation compartment is located on top of the housing to promote water condensation as well as vapor transport from the housing to condenser by air density (temperature) differences. In principle, the MOF cartridge and condenser require different thermal conditions to improve AWH during the day cycle, which need to be relatively high for water desorption and low for condensation, respectively. Therefore, by placing the condenser on top, such contradictory conditions could be compromisingly optimized with each other, of which the structure is reminiscent of rotary evaporator commonly used in chemistry laboratory. Also,

since the condenser is facing clear sky, we can configure the device design to use radiative energy dissipation to accelerate water condensation rates.

[053] MOF cartridge (bed) design. The water productivity (mass of water harvested per mass of MOF sorbents) of current AWH device at practical scale is just about ~30% of the theoretical capacity of the MOFs. For example, MOF-801 only could produce ~100 g·H₂O/kg·MOF/day while their theoretical capacity is about ~300 g·H₂O/kg·MOF/day. It is primarily due to the low SV-r that prevent maximum exposure of MOFs to the air. The highest SV-r of the previous device design is ~1.⁸ Also, as the MOF amounts in the device increased, the SV-r decreased from ~1 to ~0.5, lowering water productivity and therefore hampering the scaling-up property.

[054] In this device design, the MOF bed assembly (MOF cartridge) is designed to maintain the SV-r as 2.6, irrespective of the amounts of MOFs used in the device. For this purpose, MOF powders were pressed into the thin disc pellets with 38 mm in diameter and ~0.8 mm in height, and these pellets are stacked with porous nickel (Ni) foam discs (38 mm in diameter and 1.5 mm in height). As the porosity of the Ni foam is higher than 97%, the external air can flow or diffuse through this porous media, making the inter-facing MOF pellet surfaces exposed to the air. Also, Ni foam has the ~90 W·m⁻¹·K⁻¹ thermal conductivity and can serve as heat conductor in between MOF pellets under the solar irradiation, which is also important for efficient water desorption as the MOFs are nonconductive.

[055] Patterned surface coating of the condenser. Current MOF-assisted AWH research is mainly focused on the developments of new functional materials, and the effect of water condensation in the device has not been emphasized. However, we determined that the condenser design is also critical to improve water productivity of the device. So, we introduced a line-patterned hydrophobic (carbon nanofiber and polytetrafluoroethylene blends, CNF/PTFE) surface coating¹¹ of the condenser to improve the water productivity. In embodiments, the pattern has the same direction with gravity, to promote initial water nucleation and grow coalesced water droplets in the hydrophilic channels, and then remove condensed water by gravity rather than let water adhered over the entire metal contact due to the high surface energy. By this modification, water harvesting capacity increased from ~160g·H₂O/kg·MOF-303/day (non-coated aluminum condenser) to 250 g·H₂O/kg·MOF-303/day.

[056] One issue in comparison to the potential alternative of this invention is that current device requires external operations between the day and night cycles. For example, MOF cartridge need to be taken out from the device at night and then inserted again in the morning; hence, automated operation of this action with minimal environmental footprints is preferred.

[057] In embodiments, we install environmentally friendly actuation parts so that the transition of the device's operational modes between water sorption (night cycle) and desorption

(day cycle) can be carried out automatically. These actuation parts can be composed of solar panels and/or small batteries with minimum electrical components. In addition, in more sustainable embodiments, the invention produces water with near zero carbon emission, such actuation is performed without any electricity, including embodiments deploying thermal actuators like wax motors that are operated only by ambient temperature gradients during the day and night (**Figs. 28a-b**).

[058] Examples: MOF water harvester produces water from Death Valley desert air in ambient sunlight

[059] A water harvester based on metal-organic frameworks has been designed, constructed, and tested in two locations in California (Berkeley and Death Valley National Park). This water harvester is capable of harvesting water at a capacity of 210 and 285 g·H₂O/kg·MOF-303/day, respectively. The unique configuration of the MOF cartridge and the condenser in the harvester allows the highest efficiency of water uptake and harvesting from air without power or energy input aside from ambient sunlight. Indeed, this water harvester operate passively with double the amount of water harvested compared to our previous passive MOF water harvester.

[060] Construction of passive MOF water harvester

[061] The device was designed to have two main compartments (**Fig. 1c, Figs. 6-13**). One is the housing for the MOF cartridge and the other is the condenser. The transparent cylinder-shape housing included vacuum insulated double-wall structure to prevent conductive heat loss to environments under solar irradiation. Also, compared to the rectangular geometry that other devices used^{13,18,21}, the cylinder-shaped module can maximize the use of solar energy from the sunrise to sunset since the projected area of the cylinder body toward the sun is consistent alongside the sun trajectory (**Fig. 1d**).

[062] The condenser components are located on the top of the housing to utilize the air density (temperature) gradients inside the device as a driving force of convective vapor transport from the MOFs to the condenser. In principle, the MOF cartridge and condenser require different thermal conditions to improve AWH during the day. The cartridge needs to be heated for water desorption and the condenser cooled down for condensation, respectively. Therefore, by placing the condenser on top and separating these two compartments, such contradictory conditions could be balanced and optimized in way reminiscent of rotary evaporator commonly used in chemistry laboratories. Also, since the condenser is facing clear sky, we can expect the potential device design that use radiative energy dissipation to further accelerate water condensation^{22,23}.

[063] MOF cartridge design and assembly

[064] For efficient AWH, it is important to maximize the exposure of MOFs to environments during both adsorption and desorption steps. For example, in our former study that used MOF-

801, as the VS-r of MOF beds decreases from 1 to 0.5, water uptake capacity decreased from 230 to 210 g·H₂O/kg·MOF-801 due to the reduced accessibility of MOFs to the air, resulting in the reduced AWH capacity from 130 to 56 g·H₂O/kg·MOF-801/day¹⁸. Therefore, in this work, MOF powders were processed into the thin disc-shaped pellets (38 mm in diameter and ~0.8 mm in height), and these pellets are stacked with porous nickel (Ni) foam discs (38 mm in diameter and 1.5 mm in height) to maintain VS-r of 2.6 (**Fig. 1c** and **2a**). Since the porosity of the Ni foam is higher than 97%, the external air can flow and diffuse through this porous structure, making the MOF pellet surfaces exposed to the air. Also, Ni foam has the ~90 W·m⁻¹·K⁻¹ thermal conductivity and can serve as heat conductor in between MOF pellets under the solar irradiation, which is also important as the MOFs are typically thermal insulators with the conductivity less than 2 W/m·K²⁴⁻²⁷.

[065] Sorbent pellets were prepared by mixing the activated MOF-303 powders with graphite in different weight ratios and uniaxially pressing them under the pressure of 78 MPa for two minutes (**Figs. 14-18**). Graphite was introduced as a binder to improve both the mechanical property and the thermal conductivity of the pressed bodies, and the pellets prepared using 85 wt% MOF-303 and 15 wt% graphite (MOF₈₅-G₁₅) were further used for the device fabrication. The N₂ BET surface area of MOF₈₅-G₁₅ is 955 m²/g·MOF₈₅-G₁₅, which corresponds to 1,120 m²/g·MOF-303, showing that more than 85 % of MOF-303 surface area (1370 m²/g) was preserved under the pressing process (**Fig. 2b**). Also, MOF₈₅-G₁₅ pellets showed the characteristic water isotherm profile of MOF-303 that has the inflection point at ~12% RH, while having water uptake capacity of 29 wt% by MOF₈₅-G₁₅ (35 wt% by MOF-303) at 20% RH, which also corresponds to the 85 % capacity of MOF-303 (**Fig. 2c**). It is noteworthy that hydrophobic graphite binder was also advantageous in enhancing water resistance of the pressed pellets. When hydrophilic cellulose binders were used, the pellets were immediately dissociated in water while MOF₈₅-G₁₅ maintained their shapes more than 24 hours, showing the enhanced water resistance (**Fig. 19**).

[066] Water uptake properties of the entire MOF cartridge assembly were investigated. The cartridge was activated in an oven at 140 °C for 24 hours and the net weight change of the cartridge was measured at 25 °C and 40% RH in the environmental chamber. When 35g MOF-303 were used (42g of MOF₈₅-G₁₅), ~32 wt% increase was observed within 2 hours showing that more than 90% of the MOF-303 in MOF₈₅-G₁₅ were accessed (**Fig. 2d**). Also, the same uptake efficiencies were observed when 25 g and 45 g of MOF-303 were used respectively, indicative of the scalability of this cartridge design for water uptake (**Figs. 20a-c**).

[067] Heat and energy transfer simulation under solar irradiance

[068] Prior to the device fabrication, heat and energy transfer under solar irradiation was investigated using computer simulations. Equations of radiative, convective, and conductive heat and energy transfer were integrated for the simulations. Note that heat of water desorption from MOF₈₅-G₁₅ and latent heat release by water condensation are not considered in this computational study. As a result, under the solar irradiance of 1000 W/m² for 7 hours, the MOF bed temperature increases up to 70 °C (**Fig. 3a** and **Fig. 21**) and no greater than 2 °C temperature differences were observed over the MOF pellet stacks, showing the effective heat distribution by the cartridge design. Also, 10 °C temperature difference of MOF was observed between non-insulated single and vacuum-insulated double wall MOF housing structures. Importantly, the temperature difference between the cartridge and the condenser was maintained greater than 35 °C after 7 hours (**Fig. 3a**), showing the successful heat dissipation to environments through heat sinks and therefore the potential for water condensation.

[069] Laboratory test of the passive water harvester

[070] Based on the results of MOF cartridge water uptake experiments and energy transfer simulations, the entire device was fabricated and tested in the laboratory. First, the activated cartridge with 35 g MOF-303 (42 g MOF₈₅-G₁₅) was exposed to the 20 °C and 35% RH air for 8 hours in the environmental chamber. After this water uptake step, the cartridge was assembled and the device was exposed to 4000 K light (950 W/m²) for 7 hours monitoring the temperature and RH changes at different points of the device (**Fig. 3a,b**). Upon the light irradiance, the temperature of the MOF₈₅-G₁₅ in the cartridge started to increase instantly, reaching to the highest temperature of 67 °C. The temperature profiles of experiments and simulations showed good correspondence with each other (**Fig. 3a**), while the MOF temperature increases less rapidly than the simulation at the initial stage and the condenser temperature is slightly high. This could be attributed to the heat of water desorption and condensation at the MOF bed and the condenser respectively, which were not considered in the simulations. Importantly, spatial RH change in the device evidently showed the vapor transport from the MOF cartridge to the condenser. RH at the condenser gradually increased after the device was exposed to the light and reached to 100% within one hour (**Fig. 3b**). On the other hand, the RH near the cartridge initially increased and then decreased as water is condensed and collected, showing the water transport from the MOF₈₅-G₁₅ to the inner space of the housing, condenser, and finally collection vessel. As a result, 5.5(±0.27) g water was harvested, achieving the AWH capacity of 157(±7.8) g·H₂O/kg·MOF-303 (**Fig. 3c**).

[071] Surface modification of the condenser for facile water condensation

[072] Since water condensation is a key step, we further investigated this effect to improve the AWH capacity. One general strategy to improve the condensation rate is to modify the surface

as hydrophobic for dropwise condensations²⁸. We first tried polytetrafluoroethylene (PTFE) and carbon nanofiber-PTFE composites (CNF/PTFE) materials for hydrophobic surface treatments, using a reported spray-coating method²⁹. The hydrophobicity increased in the order of bare aluminum (Al, non-treated condenser surface) to PTFE- to CNF/PTFE-coated surfaces as confirmed by the water-air interface contact angles that are $66(\pm 2.8)^\circ$, $103(\pm 1.1)^\circ$, and $144(\pm 0.5)^\circ$, respectively (**Fig. 3d**). The AWH capacity increased from $157(\pm 7.8)$ (Al) to $220(\pm 16)$ (PTFE coating) and $210(\pm 4.7)$ g·H₂O/kg·MOF-303 (CNF/PTFE coating) (**Fig. 3c** and **Fig. 22**).

[073] While the capacity improved once the surfaces were modified, no significant difference between PTFE- and CNF/PTFE-coated condensers was observed. We hypothesized that as the hydrophobicity of the condensation surface becomes greater, the water nucleation step becomes more significant in determining the condensation rates, especially for the passive AWH. For example, condensation takes place as a serial step of nucleation, growth, droplet coalescence, and water removal by gravity²⁸. In many applications, dropwise condensation by hydrophobic surfaces is preferred since it removes the coalesced droplets quickly by gravity to minimize surface wetting that function as additional resistance for continued condensation. This implies that the nucleation step is less critical in determining the rates, which prefer hydrophilic surfaces with high surface energy³⁰. However, we believed that this initial step could be more critical in the passive AWH applications. Since the vapor is transported to the condenser under much milder conditions compared to the other applications such as hot steam generation plants³¹, there would be less gradients to drive one-directional vapor-liquid phase changes initiated by nucleation³². Therefore, since the nucleation step is important in the present case, we introduced the strip-pattern CNF/PTFE coatings on the surface alongside the direction of gravity (**Fig. 3e**). This is to promote initial water nucleation and growth of coalesced water droplets in the hydrophilic channels, and then remove merged water by gravity rather than let water adhere over the entire metal contact due to the high surface energy (**Fig. 3e**). As a result, when the hydrophobic strip-pattern was introduced to the condenser surface, the first droplet of the harvested water in collection vessel was observed within 1.5 hours which is 45 minutes faster than the other conditions, supporting that the patterned coating could accelerate the condensation rates. Also, the AWH capacity increased from $210(\pm 4.7)$ to $248(\pm 7.2)$ g·H₂O/kg·MOF-303 (**Fig. 3c**).

[074] **Water harvesting test in the field: Berkeley, California, United States (37.8715° N, 122.2730° W)**

[075] Our passive water harvester was tested outdoors in Berkeley on two different days, when the average ambient temperature (T_{avg}) during the day cycle was relatively higher (June 2,

2022) and lower (June 10, 2022) than the indoor laboratory conditions (25 °) (**Fig. 4a, Figs. 23a-d**). The T_{avg} and the average solar irradiance intensity (I_{avg}) were 19.6 °C and 620 W/m², and 31.5 °C and 720 W/m², respectively. During the night cycles, the activated MOF cartridge was left outdoor, and the day cycle tests were performed for 8 hours from 8:30 to 16:30 monitoring the temperature, RH, and solar irradiance (**Fig. 4b,c**).

[076] Upon the exposure to sunlight, the spatial temperature and RH of the device changed with the similar profiles observed in the laboratory tests (**Figs. 3a and 4b**) and the device successfully harvested water on both days, achieving AWH capacity of 285 and 210 g·H₂O/kg·MOF-303/day on June 2 and June 10, respectively (**Fig. 4d**). The June 2 result showed even higher water productivity than the indoor laboratory tests, which could be attributed to improved condensation owing to the lower ambient temperature and therefore more efficient both conductive and convective (by outdoor airflow) heat release to the atmosphere. In addition, during the June 10 test, the condenser temperature increased up to 43 °C; significantly higher than the temperature observed in the laboratory, but water was successfully harvested.

[077] Given that, in our previous study that tested the previous version of passive device in Arizona (AZ) desert, condensation was not observed at a similar condenser (42 °C) and atmosphere (35 °C of the peak during the day cycle) temperature conditions¹⁸, indicating the importance of the following design considerations for the passive AWH device: (1) choosing condenser materials with good wettability to attract water molecules for surface adhesion since the previous device used poly(methyl methacrylate) plastics as the condenser, and (2) guiding humid air into the confined space so that the air condition reaches to the dew point (100% RH) and maintain this condition effectively, an aspect was driven by air density differences between the housing and the condenser in this study (**Fig. 1a**).

[078] **Water harvesting test in the field: Death Valley, Nevada and California, United States (36.5319° N, -116.5455° W and 36.4506 ° N, -116.8523° W)**

[079] The device was further tested in the Death Valley areas in mid-summer during the month of August 2022, to assess the AWH even under extremely dry and hot air conditions. The tests were performed for full three night-and-day cycles; namely, two cycles near the east boundary of the Death Valley National Park (36.5319° N, -116.5455° W) from August 19 to August 21, 2022 and another cycle at the Furnace Creek (36.4506 ° N, -116.8523° W) from August 22 to August 23, 2022, the latter being the driest location of the Death Valley due to the elevation below sea level at the center of the valley (**Fig. 5 and Figs. 24a– 27b**).

[080] During these tests, the lowest day-time peak temperature near the ground was 56 °C (August 21) and the highest night-time RH_{avg} was 26%. Especially in the Furnace Creek location, the RH_{avg} during the night was just 14% with the peak of 21% at around 4:30 AM (**Fig.**

5b). Even under this extreme weather condition that the condenser temperature reached to 65 °C, the device successfully harvested water from air with the AWH capacity of 114 g·H₂O/kg·MOF-303/day. Considering all these tests, the productivity of the device was 210 g·H₂O/kg·MOF-303/day in the Death Valley area. For comparison, the AWH capacities are summarized in **Fig. 5c** and **d** as a function of RH_{avg} and T_{avg} during the night and day cycles, respectively. Strong relationships are evident between these two factors and AWH capacity, confirming that both humidity and temperature conditions are critical in determining the efficiency of passive MOF harvesting. These results also demonstrate the importance of condensation process to improve passive water harvesting capacity.

[081] Summary

[082] A passive water harvester based on MOF-303 has been designed and configured to achieve the highest efficiency among passive designs. A water harvesting capacity of 280 g·H₂O/kg·MOF-303/day with only ambient sunlight and no power or other energy input. The MOF cartridge design and the condenser surface treatment were key features in achieving high water harvesting efficiency especially when tested in the field (Death Valley National Park). Also, harvesting capacity per unit area is also important for passive AWH to minimize environmental footprint. In this regard, owing to the compact and modular design of the device, water productivity of 200 g·H₂O/m²/day was achieved, which is three folds higher than our previous passive device design (65 g·H₂O/m²/day)¹⁸.

[083] Methods

[084] *MOF-303 synthesis and MOF₈₅-G₁₅ preparation:* MOF-303 was synthesized using the method previously reported¹⁸. In brief, 8.072 g (51.7 mmol) of 3,5-pyrazoledicarboxylic acid (H₂PZDC) was dissolved in 420 mL of DI water slowly adding 30 mL of 2.6 M NaOH solution by stirring for 10 min. The solution was sonicated for 5 min. 12.5 g (51.7 mmol) of aluminum chloride hexahydrate (AlCl₃·6H₂O) was added to the solution by stirring for 5 min and heated at 100 °C for 24 hours. The precipitates were divided into 50 mL tubes and washed with DI water by centrifugation three times over the course of 24 hours for three days, followed by washing with methanol over the course of 24 hours for three days. The samples were air-dried for 24 hours and activated at 150 °C either under the vacuum (for 10 hours, powders) or in the convection oven (for two days, MOF pellets). For MOF₈₅-G₁₅ preparation, the activated MOF-303 was mixed with 15 wt% graphite. The mixture was grinded in mortar, and pressed using the bench top hydraulic press (Carver, 4350 model) with 38 mm circular-shaped press dye at the pressure of 78 MPa for 2 min.

[085] *Device design and fabrication:* The device parts were designed using SOLIDWORKS 3D CAD software. The details of the part drawings with dimensions are available in Information

(Figs. 4-7). The MOF housing was fabricated by co-centering two PMMA acrylic tubes with custom-made acrylic cap and flange using acrylic glue to form vacuum layer. One 1/8 FNPT threaded port was made on the outer tubing shell to be connected to vacuum pump, and the vacuum was hold using the valve during the test (Fig. 4). The MOF cartridge tray slot was custom machined using Al tubing (38 mm ID × 44 mm OD) and coated with conductive carbon paint (MG Chemicals, 838AR) using a paint brush. The other parts of the device were 3D printed using Markforged Onyx One printer with micro carbon filled nylon (Onyx™) filaments. Two aluminum heat sinks (40 mm × 100 mm × 20 mm) were used as the condenser.

[086] *PTFE and CNF/PTFE surface coating of the aluminum heat sinks:* Hydrophobic coating of the Al condenser surfaces were conducted using the previously reported method²⁹. In brief, for CNF/PTFE coating, 180 mg of PTFE powder (Sigma Aldrich, cat#: 430935) and 20 mg of CNF (Sigma Aldrich, cat#: 719781) was mixed with 20 g of dichloromethane (DCM) and dispersed using the probe sonicator for 2 minutes. This CNF/PTFE/DCM suspension was loaded in VL double-action airbrush (Paasche) and sprayed over the heat sink surfaces. The heat sink was heated at 400 °C for 30 min for CNT/PTFE annealing on the surface and then cooled down to room temperature. For PTFE coating, the same procedure was used except for only using CNF in preparing the suspension solution. For the patterned CNF/PTFE coating, the condenser surface was masked using 3 mm thick masking tapes before spraying CNF/PTFE solution. The masking tapes were removed, and the condenser was annealed as described earlier.

[087] *Contact angle measurements:* Water-air interface contact angles were measured using the custom-made measurement apparatus. Using the micropipette, 10 µl of DI water was placed on the subject surfaces and the droplet photographs were taken using the camera. The contact angles were analyzed using the contact angle pug-in of ImageJ software.

[088] *Lab tests of the device:* Prior to the tests, the MOF cartridge was activated in an oven at 140 °C for more than 16 hours and incubated in the SH-242 ESPEC environmental test chamber with 20 °C and 35% RH air conditions for 8 hours. After this, the cartridge was assembled into the device and exposed to 4000 K light with 45° irradiation angle. Light intensity was adjusted to be 950 W/m² using the Hukseflux LP02-C pyranometer connected to the LI-19 data logger. Each indoor test was carried out for 7 hours, monitoring the temperature and RH changes of the MOF₈₅-G₁₅, the case (air gap between MOF cartridge and housing), and the condenser.

[089] *Field tests of the passive AWH device:* The MOF cartridge was activated in an oven at 140 °C for more than 16 hours. During the night cycles, the MOF cartridge was left outdoors over-night for atmospheric water uptake. For the day cycles, the cartridge was assembled, and the device was set facing the south pole to maximize the use of sunlight as described in Fig. 1d. The tests were carried out from 8:30 to 16:00 in Berkeley area and from sunset to sunrise in the

Death Valley area respectively, monitoring the temperature and RH changes. The exact locations of each test are followings: June 2 and June 8 2022 (37.8715° N, 122.2730° W), from August 19 to August 21, 2022 (36.5319° N, -116.5455° W), and from August 22 to August 23, 2022 (36.4506 ° N, -116.8523° W).

[090] References

- [091] 1. The Sustainable Development Goals Report. *United Nations* **2018**.
- [092] 2. State of Global Water Resources 2021. *World Metrological Organization* **2022**.
- [093] 3. Mekonnen, M. M.; Hoekstra, A. Y., Four billion people facing severe water scarcity. *Science Advances* **2016**, 2 (2), e1500323.
- [094] 4. Famiglietti, J. S., The global groundwater crisis. *Nature Climate Change* **2014**, 4 (11), 945-948.
- [095] 5. Hoekstra, A. Y.; Mekonnen, M. M., The water footprint of humanity. *Proceedings of the National Academy of Sciences* **2012**, 109 (9), 3232-3237.
- [096] 6. Peeters, R.; Vanderschaeghe, H.; Rongé, J.; Martens, J. A., Energy performance and climate dependency of technologies for fresh water production from atmospheric water vapour. *Environmental Science: Water Research & Technology* **2020**, 6 (8), 2016-2034.
- [097] 7. Lord, J.; Thomas, A.; Treat, N.; Forkin, M.; Bain, R.; Dulac, P.; Behroozi, C. H.; Mamutov, T.; Fongheiser, J.; Kobilansky, N.; Washburn, S.; Truesdell, C.; Lee, C.; Schmaelzle, P. H., Global potential for harvesting drinking water from air using solar energy. *Nature* **2021**, 598 (7882), 611-617.
- [098] 8. Lu, H.; Shi, W.; Guo, Y.; Guan, W.; Lei, C.; Yu, G., Materials Engineering for Atmospheric Water Harvesting: Progress and Perspectives. *Advanced Materials* **2022**, 34 (12), 2110079.
- [099] 9. Hanikel, N.; Prévot, M. S.; Fathieh, F.; Kapustin, E. A.; Lyu, H.; Wang, H.; Diercks, N. J.; Glover, T. G.; Yaghi, O. M., Rapid Cycling and Exceptional Yield in a Metal-Organic Framework Water Harvester. *ACS Central Science* **2019**, 5 (10), 1699-1706.
- [0100] 10. Almassad, H. A.; Abaza, R. I.; Siwwan, L.; Al-Maythality, B.; Cordova, K. E., Environmentally adaptive MOF-based device enables continuous self-optimizing atmospheric water harvesting. *Nature Communications* **2022**, 13 (1), 4873.
- [0101] 11. Kim, H.; Yang, S.; Rao, S. R.; Narayanan, S.; Kapustin, E. A.; Furukawa, H.; Umans, A. S.; Yaghi, O. M.; Wang, E. N., Water harvesting from air with metal-organic frameworks powered by natural sunlight. *Science* **2017**, 356 (6336), 430-434.
- [0102] 12. Deng, F.; Chen, Z.; Wang, C.; Xiang, C.; Poredoš, P.; Wang, R., Hygroscopic Porous Polymer for Sorption-Based Atmospheric Water Harvesting. *Advanced Science* **2022**, 9 (33), 2204724.

- [0103] 13. LaPotin, A.; Zhong, Y.; Zhang, L.; Zhao, L.; Leroy, A.; Kim, H.; Rao, S. R.; Wang, E. N., Dual-Stage Atmospheric Water Harvesting Device for Scalable Solar-Driven Water Production. *Joule* **2021**, 5 (1), 166-182.
- [0104] 14. Shan, H.; Li, C.; Chen, Z.; Ying, W.; Poredoš, P.; Ye, Z.; Pan, Q.; Wang, J.; Wang, R., Exceptional water production yield enabled by batch-processed portable water harvester in semi-arid climate. *Nature Communications* **2022**, 13 (1), 5406.
- [0105] 15. Song, Y.; Xu, N.; Liu, G.; Qi, H.; Zhao, W.; Zhu, B.; Zhou, L.; Zhu, J., High-yield solar-driven atmospheric water harvesting of metal-organic-framework-derived nanoporous carbon with fast-diffusion water channels. *Nature Nanotechnology* **2022**, 17 (8), 857-863.
- [0106] 16. Wang, J.; Dang, Y.; Meguerdichian, A. G.; Dissanayake, S.; Kankanam-Kapuge, T.; Bamonte, S.; Tobin, Z. M.; Achola, L. A.; Suib, S. L., Water Harvesting from the Atmosphere in Arid Areas with Manganese Dioxide. *Environmental Science & Technology Letters* **2020**, 7 (1), 48-53.
- [0107] 17. Guo, Y.; Guan, W.; Lei, C.; Lu, H.; Shi, W.; Yu, G., Scalable super hygroscopic polymer films for sustainable moisture harvesting in arid environments. *Nature Communications* **2022**, 13 (1), 2761.
- [0108] 18. Fathieh, F.; Kalmutzki, M. J.; Kapustin, E. A.; Waller, P. J.; Yang, J.; Yaghi, O. M., Practical water production from desert air. *Science Advances* **2018**, 4 (6), eaat3198.
- [0109] 19. Hanikel, N.; Pei, X.; Chheda, S.; Lyu, H.; Jeong, W.; Sauer, J.; Gagliardi, L.; Yaghi, O. M., Evolution of water structures in metal-organic frameworks for improved atmospheric water harvesting. *Science* **2021**, 374 (6566), 454-459.
- [0110] 20. Zheng, Z.; Hanikel, N.; Lyu, H.; Yaghi, O. M., Broadly Tunable Atmospheric Water Harvesting in Multivariate Metal-Organic Frameworks. *Journal of the American Chemical Society* **2022**.
- [0111] 21. Kim, H.; Rao, S. R.; Kapustin, E. A.; Zhao, L.; Yang, S.; Yaghi, O. M.; Wang, E. N., Adsorption-based atmospheric water harvesting device for arid climates. *Nature Communications* **2018**, 9 (1), 1191.
- [0112] 22. Catalanotti, S.; Cuomo, V.; Piro, G.; Ruggi, D.; Silvestrini, V.; Troise, G., The radiative cooling of selective surfaces. *Solar Energy* **1975**, 17 (2), 83-89.
- [0113] 23. Raman, A. P.; Anoma, M. A.; Zhu, L.; Rephaeli, E.; Fan, S., Passive radiative cooling below ambient air temperature under direct sunlight. *Nature* **2014**, 515 (7528), 540-544.
- [0114] 24. Huang, B. L.; Ni, Z.; Millward, A.; McGaughey, A. J. H.; Uher, C.; Kaviani, M.; Yaghi, O., Thermal conductivity of a metal-organic framework (MOF-5): Part II. Measurement. *International Journal of Heat and Mass Transfer* **2007**, 50 (3), 405-411.

- [0115] 25. Erickson, K. J.; Léonard, F.; Stavila, V.; Foster, M. E.; Spataru, C. D.; Jones, R. E.; Foley, B. M.; Hopkins, P. E.; Allendorf, M. D.; Talin, A. A., Thin Film Thermoelectric Metal–Organic Framework with High Seebeck Coefficient and Low Thermal Conductivity. *Advanced Materials* **2015**, 27 (22), 3453-3459.
- [0116] 26. Gunatilleke, W. D. C. B.; Wei, K.; Niu, Z.; Wojtas, L.; Nolas, G.; Ma, S., Thermal conductivity of a perovskite-type metal–organic framework crystal. *Dalton Transactions* **2017**, 46 (39), 13342-13344.
- [0117] 27. Babaei, H.; DeCoster, M. E.; Jeong, M.; Hassan, Z. M.; Islamoglu, T.; Baumgart, H.; McGaughey, A. J. H.; Redel, E.; Farha, O. K.; Hopkins, P. E.; Malen, J. A.; Wilmer, C. E., Observation of reduced thermal conductivity in a metal-organic framework due to the presence of adsorbates. *Nature Communications* **2020**, 11 (1), 4010.
- [0118] 28. Goswami, A.; Pillai, S. C.; McGranaghan, G., Surface modifications to enhance dropwise condensation. *Surfaces and Interfaces* **2021**, 25, 101143.
- [0119] 29. Donati, M.; Lam, C. W. E.; Milionis, A.; Sharma, C. S.; Tripathy, A.; Zendeli, A.; Poulikakos, D., Dropwise Condensation: Sprayable Thin and Robust Carbon Nanofiber Composite Coating for Extreme Jumping Dropwise Condensation Performance (Adv. Mater. Interfaces 1/2021). *Advanced Materials Interfaces* **2021**, 8 (1), 2170002.
- [0120] 30. Cha, H.; Vahabi, H.; Wu, A.; Chavan, S.; Kim, M.-K.; Sett, S.; Bosch, S. A.; Wang, W.; Kota, A. K.; Miljkovic, N., Dropwise condensation on solid hydrophilic surfaces. *Science Advances* **2020**, 6 (2), eaax0746.
- [0121] 31. Tanner, D. W.; Potter, C. J.; Pope, D.; West, D., Heat transfer in dropwise condensation—Part I The effects of heat flux, steam velocity and non-condensable gas concentration. *International Journal of Heat and Mass Transfer* **1965**, 8 (3), 419-426.
- [0122] 32. Hntsberger, J. R., Surface Energy, Wetting and Adhesion. *The Journal of Adhesion* **1981**, 12 (1), 3-12.

CLAIMS

1. A scalable and passive sorbent assisted atmospheric water harvester device that uses the sorbent to transform water in air into drinkable water, only using natural sunlight and ambient temperatures.
2. The device of claim 1, wherein the sorbent is selected from a metal-organic framework (MOF), which maybe aluminum-based, a covalent organic framework (COF), which may be boron or nitrogen-based, and a zeolite.
3. The device of claim 1, comprising optimization processes of water sorption, desorption and condensation processes at device scale to improve water harvesting capacity.
4. The device of claim 1, configured to provide drinking, agricultural, and municipal water, or for sorption-driven heat exchangers, humidity control for many industrial processes, heat pumps, etc.
5. The device of claim 1, configured to provide up-scalable MOF-assisted passive atmospheric water harvesting (AWH), comprising components: (a) a MOF bed providing a relatively increased the ratio of volume-to-surface area (SV-r), (b) a MOF bed assembly (MOF cartridge) configured to efficiently use natural sunlight, and (c) a condenser configured to accelerate water condensation properties, wherein the components can contribute synergistically to effective water sorption, desorption, and condensation for AWH at practical scale.
6. The device of claim 5, configured to improving the scalability of the device, wherein the MOF cartridge is designed and configured to have the constant SV-r irrespective of MOF amounts integrated into the device; for example, in particular embodiments, this device can produce water up to ~285 g•H₂O/kg•MOF-303/day.
7. The device of claim 5, comprising a housing for the MOF bed cartridge and a condenser compartment,
wherein the housing is of cylinder-shape and has a vacuum insulated double-wall structure to prevent conductive heat loss to the environment, wherein the projected area of the cylinder body toward the solar irradiation is consistent alongside the sun trajectory, maximizing the use of solar energy from the sun rise to the sun set;

wherein the condensation compartment is located on top of the housing to promote water condensation as well as vapor transport from the housing to condenser by air density (temperature) differences;

wherein the MOF cartridge and condenser may require different thermal conditions to improve AWH during the day cycle;

wherein the condenser may face clear sky, to use radiative energy dissipation to accelerate water condensation rates in the future.

8. The device of claim 5 or 7, comprising a MOF bed assembly (cartridge) is configured maintain the SV-r as 2.6, irrespective of the amounts of MOFs used in the device.

9. The device of claim 5 or 7, comprising a MOF bed assembly (cartridge) is configured maintain the SV-r as 2.6, irrespective of the amounts of MOFs used in the device, wherein the cartridge comprises MOF powders pressed into the thin disc pellets with 38 mm in diameter and ~0.8 mm in height, and these pellets are stacked with porous nickel (Ni) foam discs (38 mm in diameter and 1.5 mm in height).

10. The device of claim 5 or 8, comprising a MOF bed assembly (cartridge) is configured maintain the SV-r as 2.6, irrespective of the amounts of MOFs used in the device, wherein the cartridge comprises MOF powders pressed into the thin disc pellets with 38 mm in diameter and ~0.8 mm in height, and these pellets are stacked with porous nickel (Ni) foam discs (38 mm in diameter and 1.5 mm in height), wherein the porosity of the Ni foam is higher than 97%, the external air can flow or diffuse through this porous media, making the inter-facing MOF pellet surfaces exposed to the air, and the Ni foam has the $\sim 90 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ thermal conductivity and can serve as heat conductor in between MOF pellets under the solar irradiation.

11. The device of claim 5 or 7, configured to comprise a patterned surface coating of the condenser to improve the water productivity.

12. The device of claim 5 or 7, configured to comprise a line-patterned hydrophobic surface coating of the condenser to improve the water productivity, the coating selected from carbon nanofiber and polytetrafluoroethylene blends (CNF/PTFE).

13. The device of claim 5 or 7, configured to comprise a line-patterned hydrophobic surface coating of the condenser to improve the water productivity, wherein the pattern has the same

direction with gravity, to promote initial water nucleation and grow coalesced water droplets in the hydrophilic channels, and then remove condensed water by gravity rather than let water adhered over the entire metal contact due to the high surface energy.

14. The device of claim 5 or 7, configured to comprise environmentally-friendly actuators, so that the transition of the device's operational modes between water sorption (night cycle) and desorption (day cycle) can be carried out automatically, such as configured with solar panels and/or small batteries with minimum electrical components.

15. The device of claim 5 or 7, wherein actuation is performed without any electricity, including embodiments deploying thermal actuators like wax motors that are operated only by ambient temperature gradients during the day and night.

16. The device of claim 1, configured essentially as shown in Figs. 1a-c.

17. The device of claim 1, configured essentially as shown in Fig. 2a.

18. The device of claim 1, configured essentially as shown in Fig. 4a-b.

19. The device of claim 1, configured essentially as shown in Fig. 6.

20. The device of claim 1, configured essentially as shown in Fig. 7.

21. The device of claim 1, configured essentially as shown in Fig. 8.

22. The device of claim 1, configured essentially as shown in Figs. 9a-b.

23. The device of claim 1, configured essentially as shown in Fig. 10.

25. The device of claim 1, configured essentially as shown in Figs. 11a-b, 12 or 13.

25. The device of claim 1, configured essentially as shown in Fig. 28.

26. A method of harvesting water comprising operating a device of claim 1, 5 or 7, herein to capture and collect water from air.

Fig. 1b

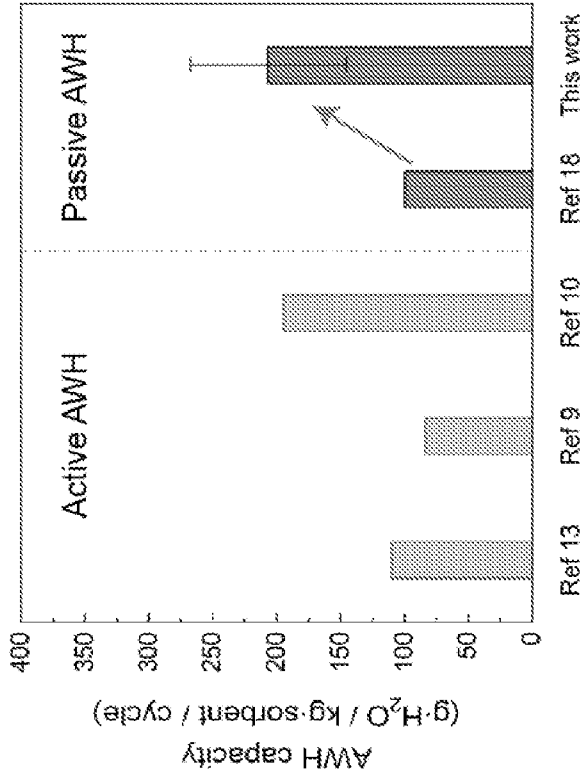


Fig. 1a

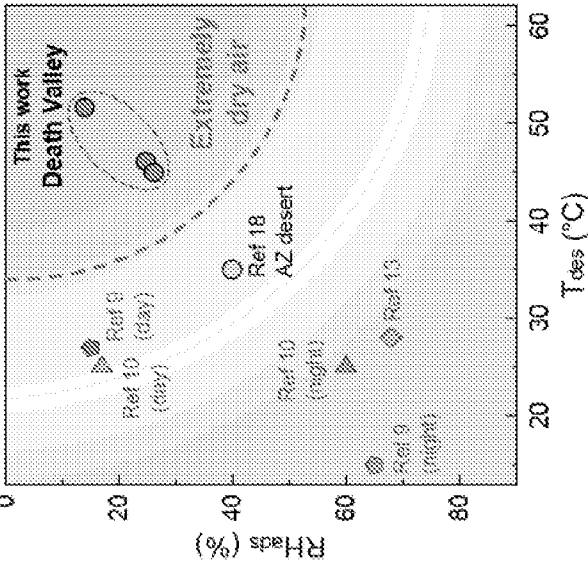


Fig. 1c

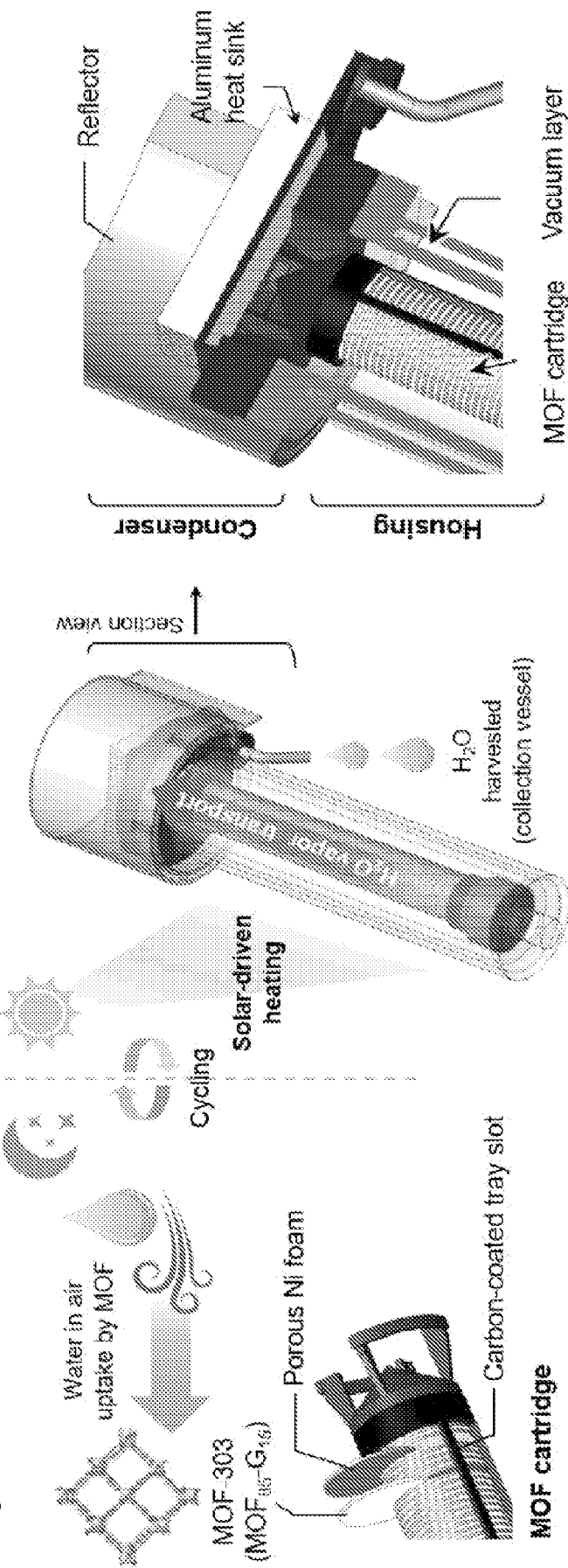


Fig. 1d

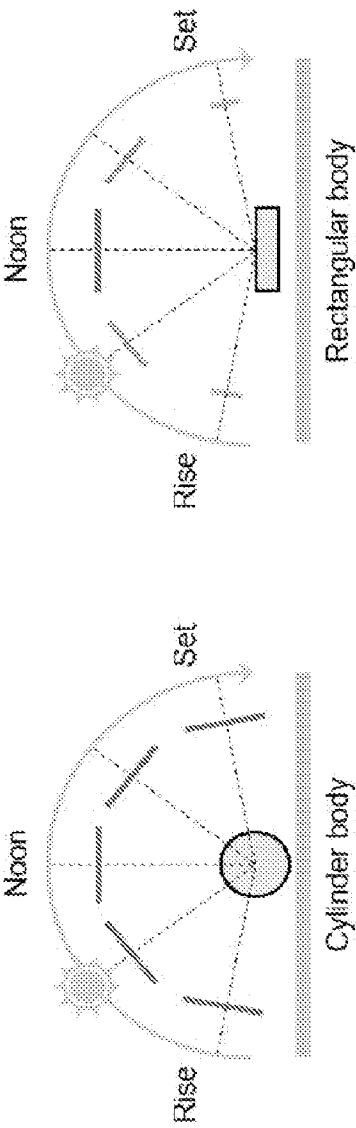


Fig. 2a

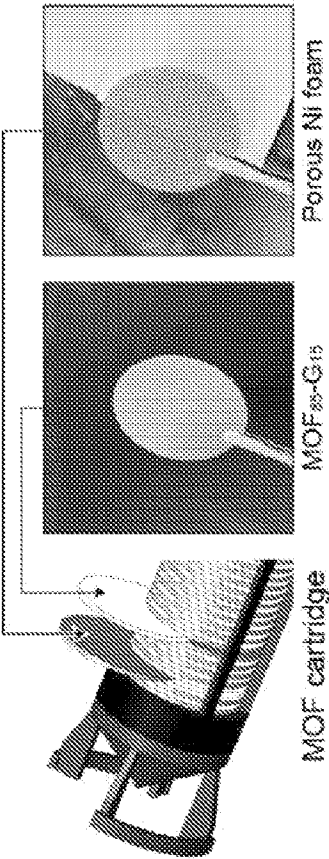


Fig. 2b

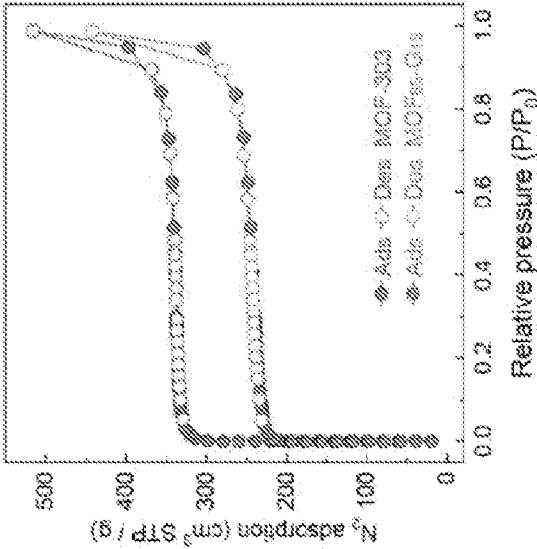


Fig. 2c

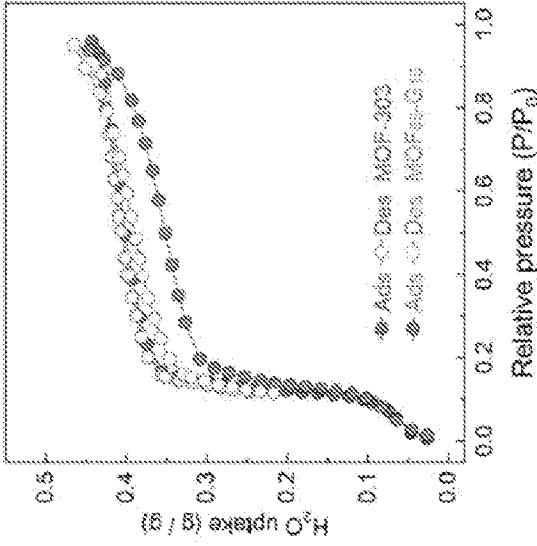
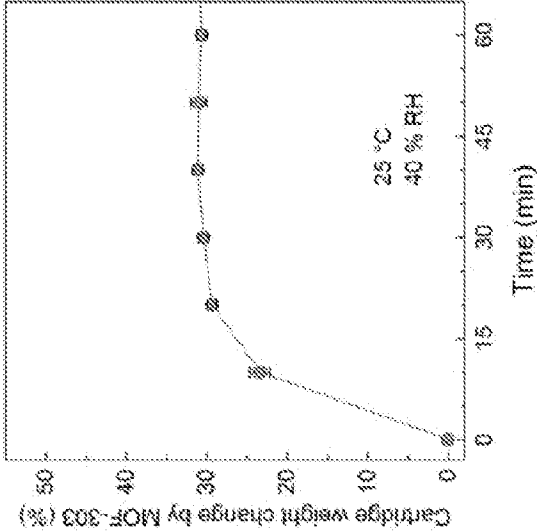


Fig. 2d



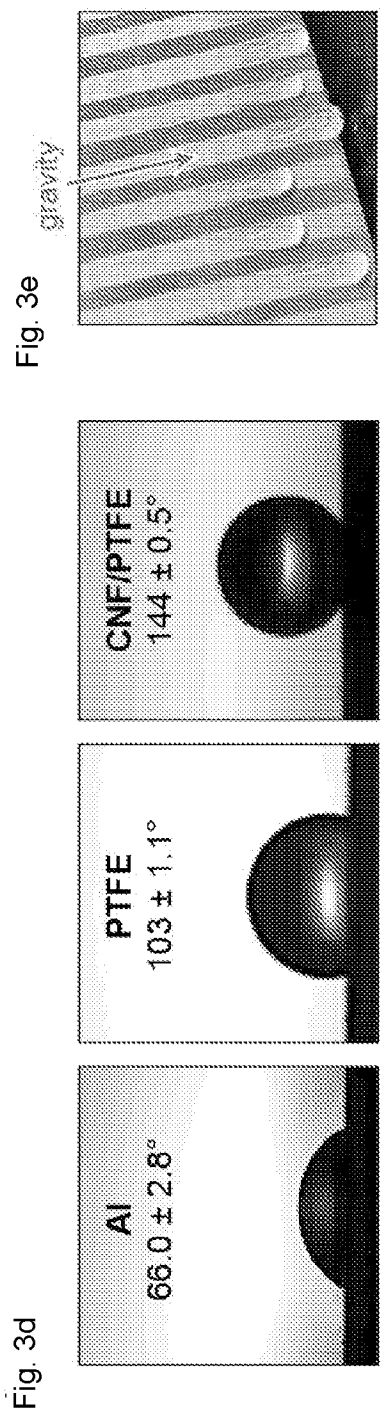
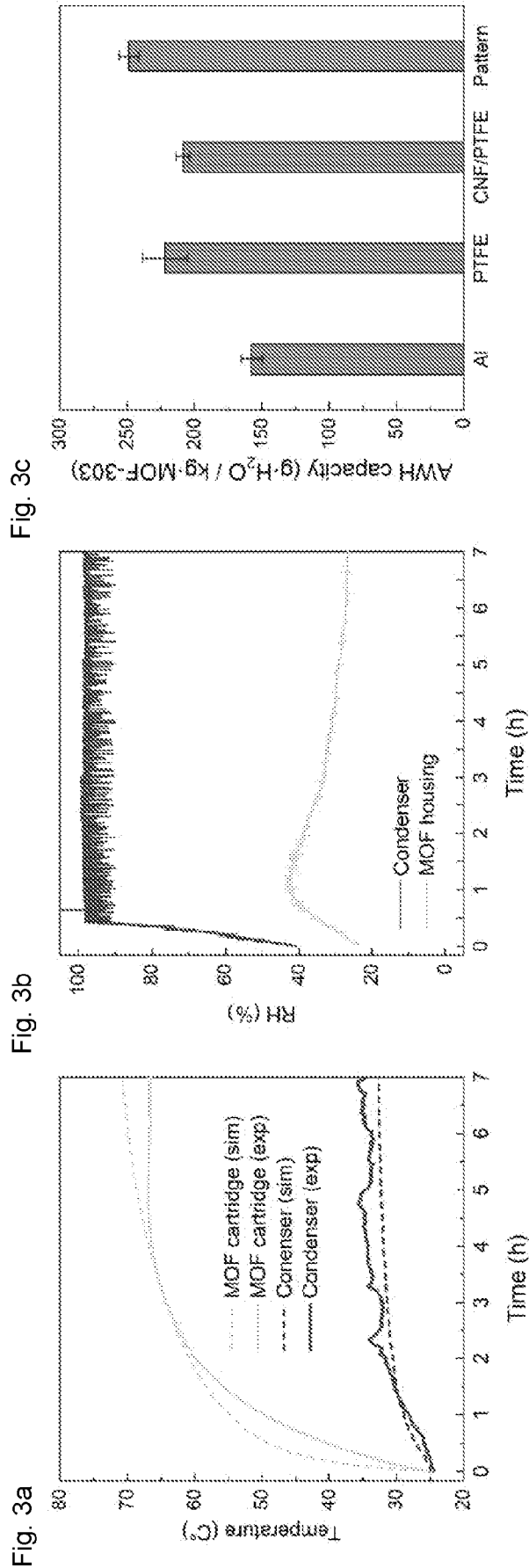


Fig. 4a

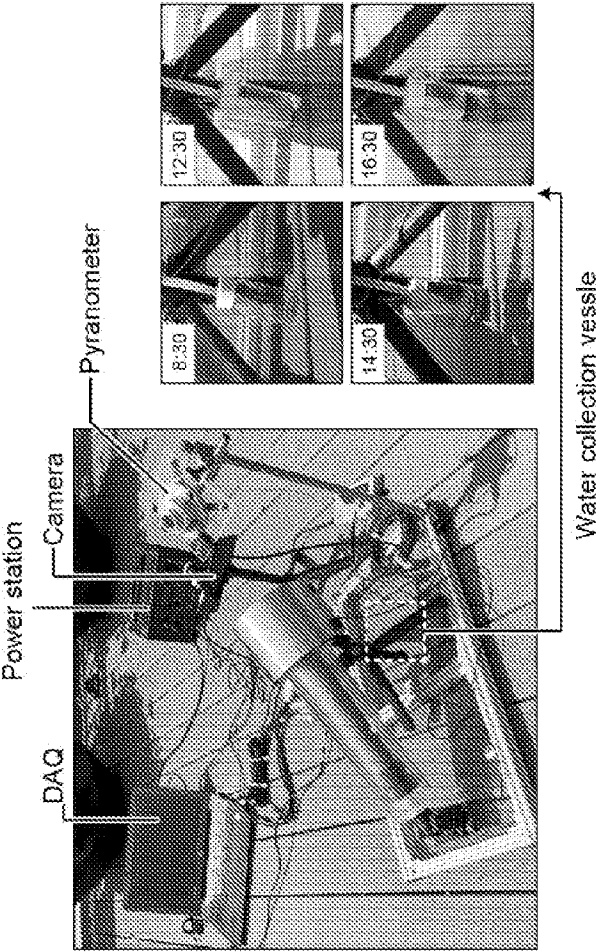


Fig. 4c

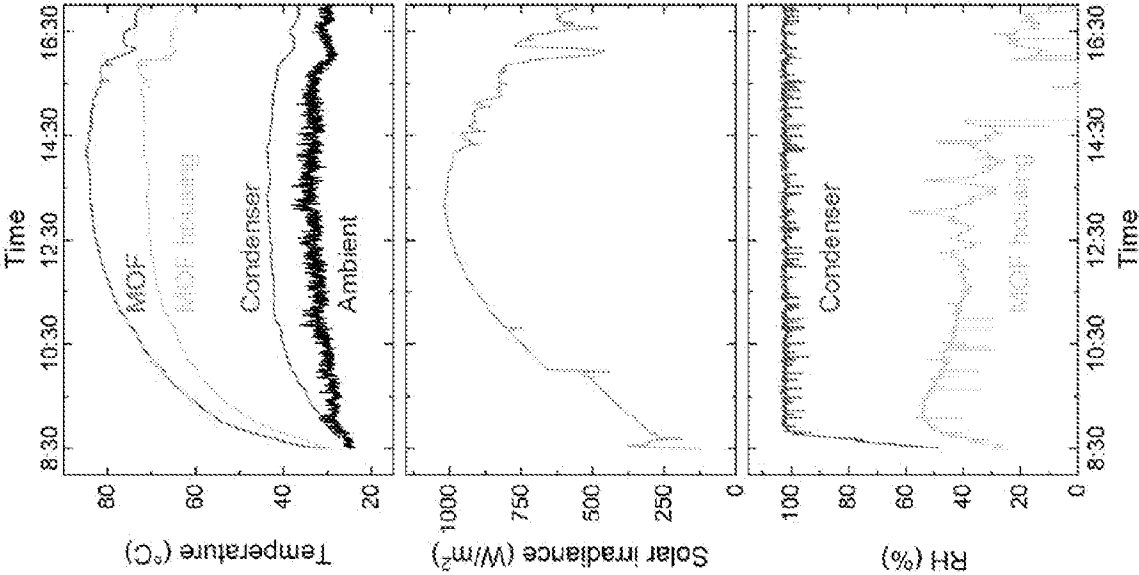


Fig. 4b

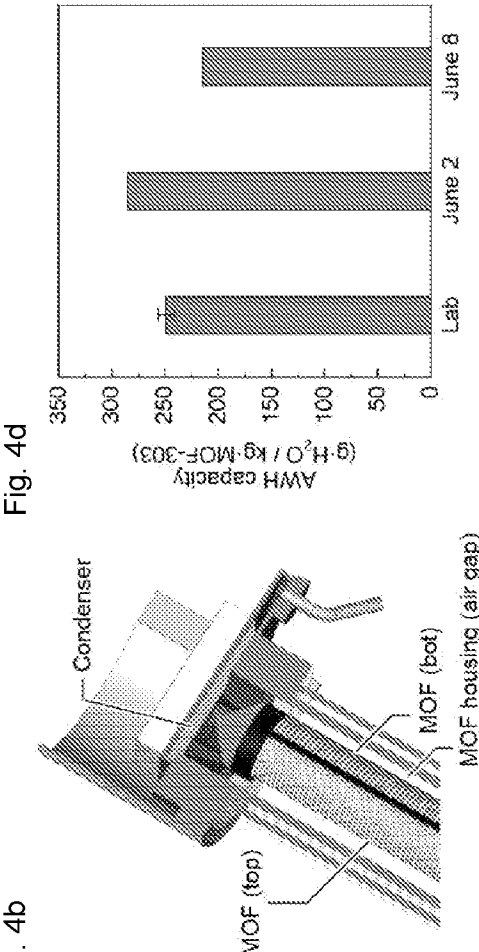


Fig. 5a

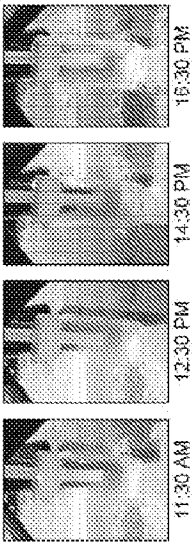
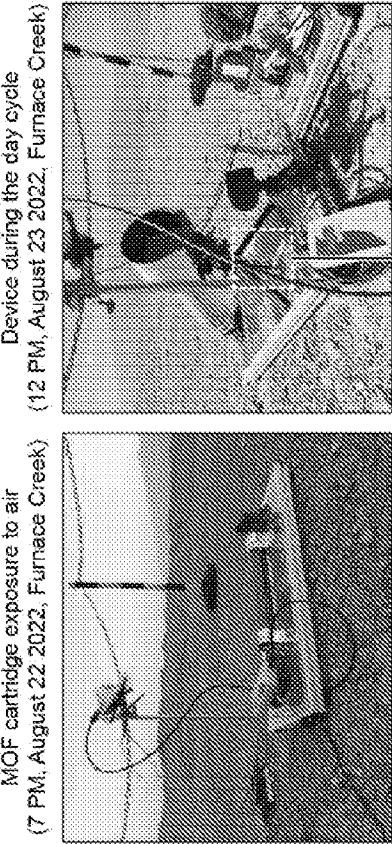


Fig. 5b

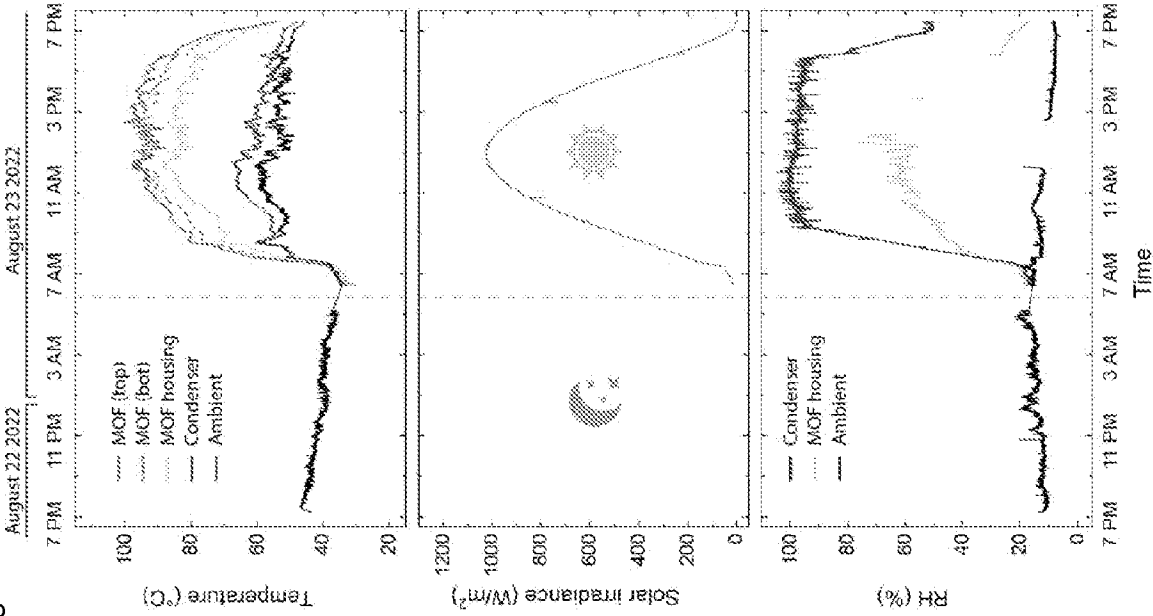


Fig. 5c

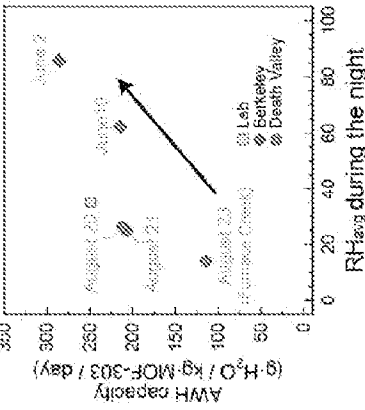


Fig. 5d

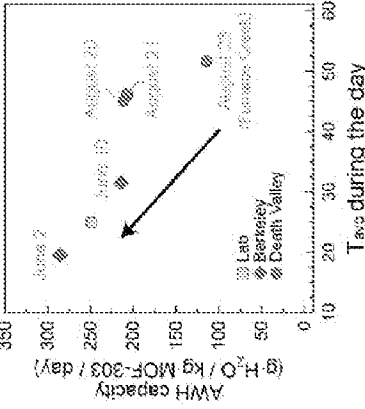


Fig. 6

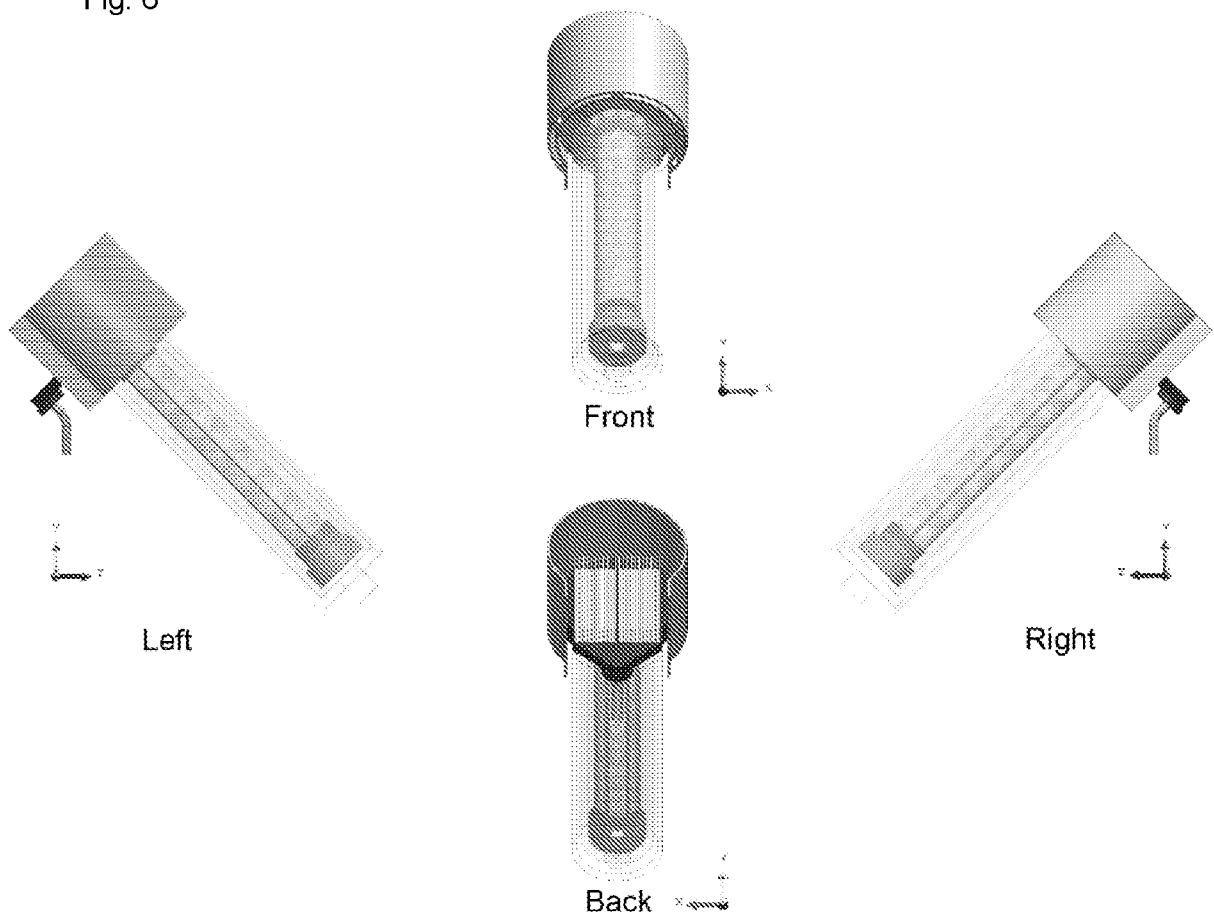


Fig. 7

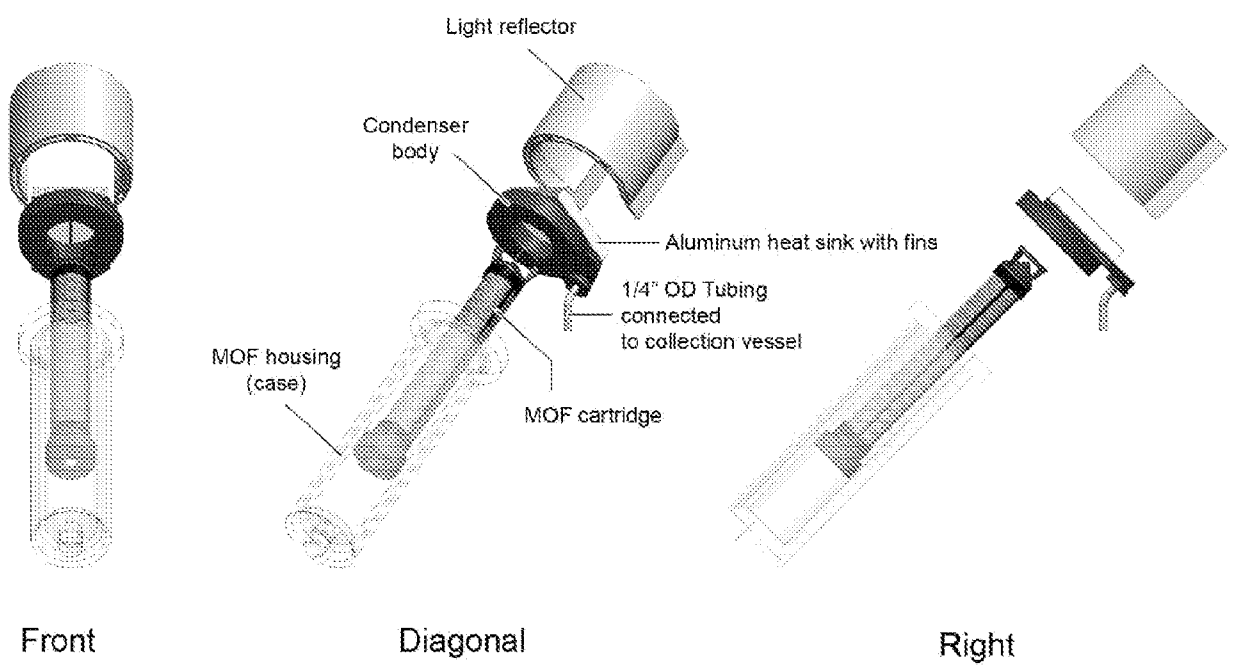


Fig. 8

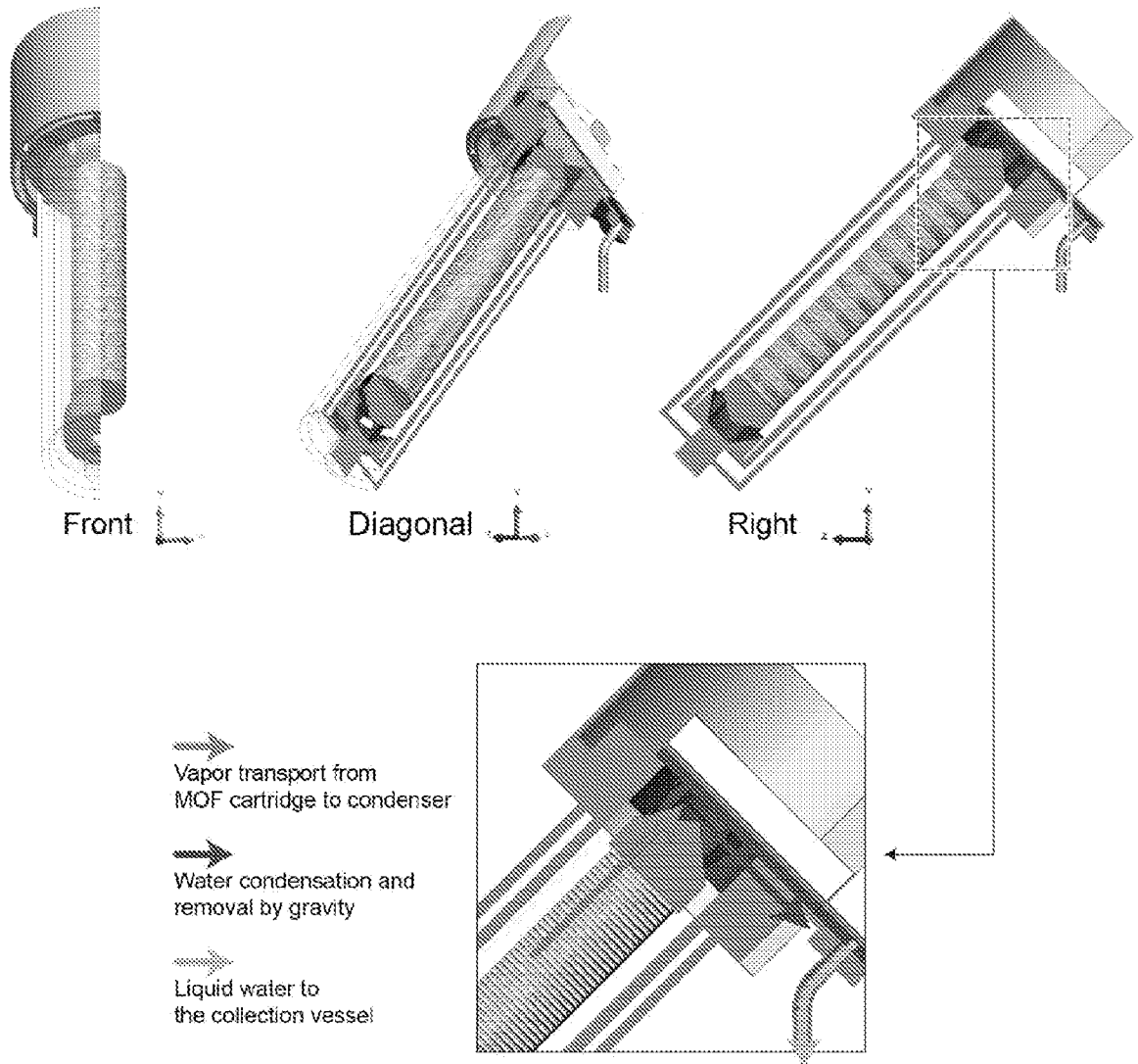


Fig. 9a

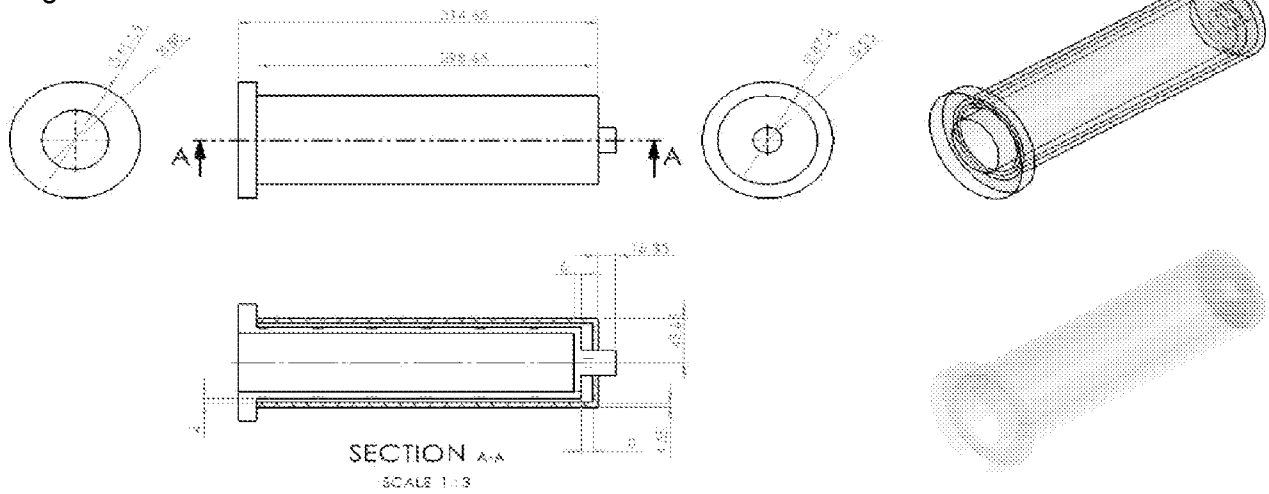


Fig. 9b

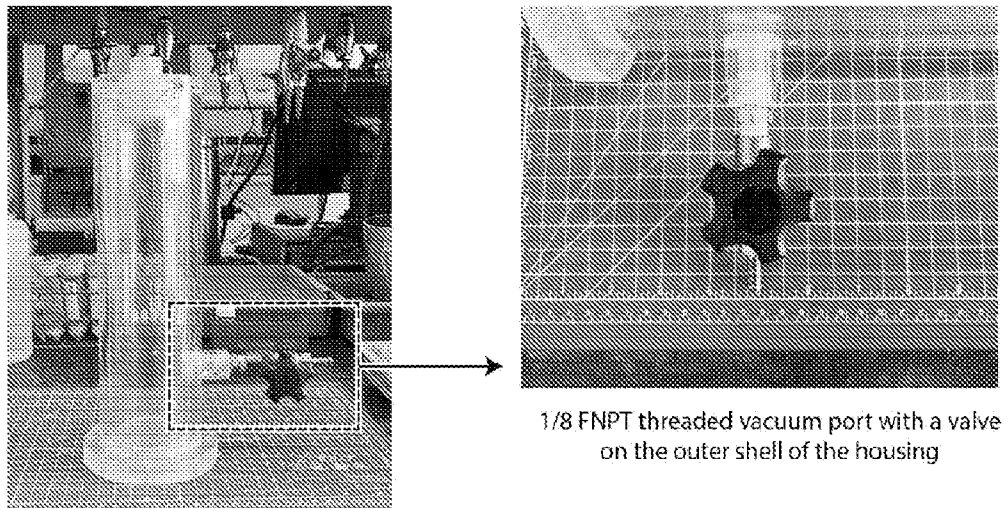


Fig. 10

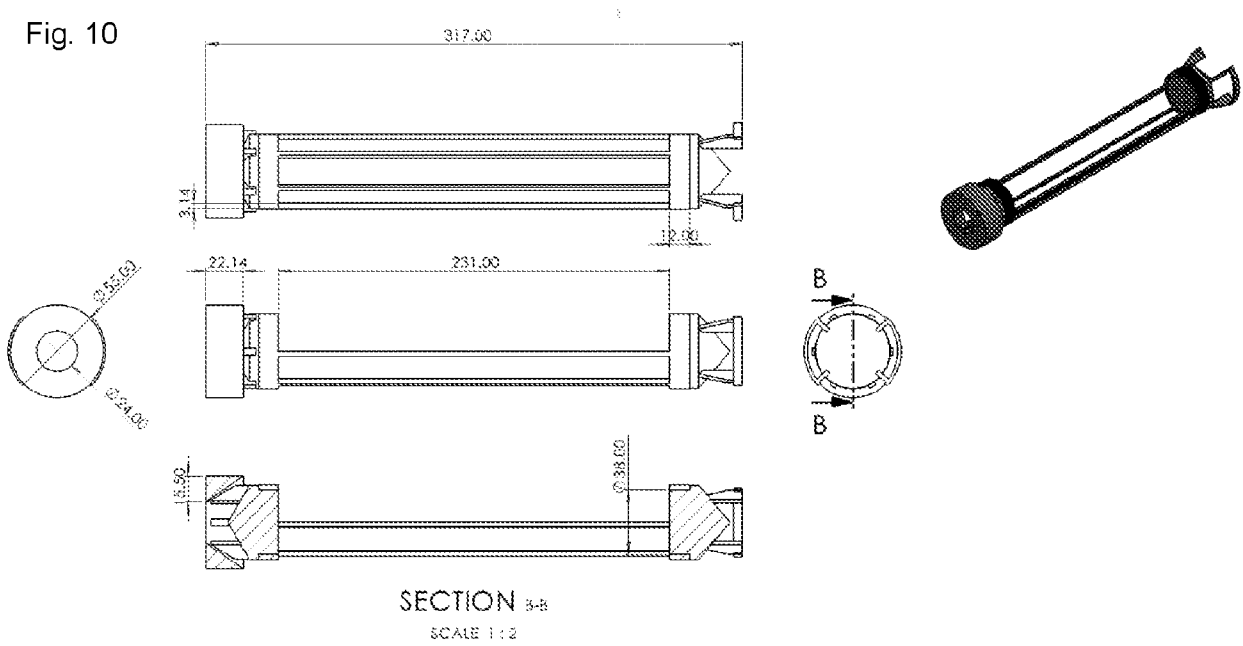


Fig. 11a

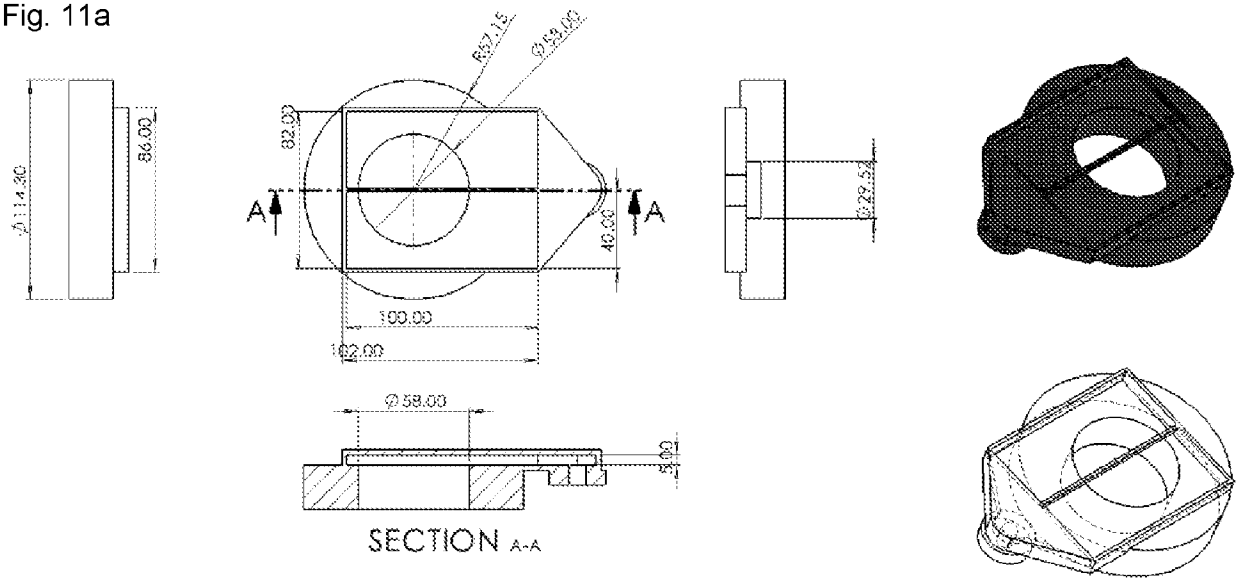


Fig. 11b

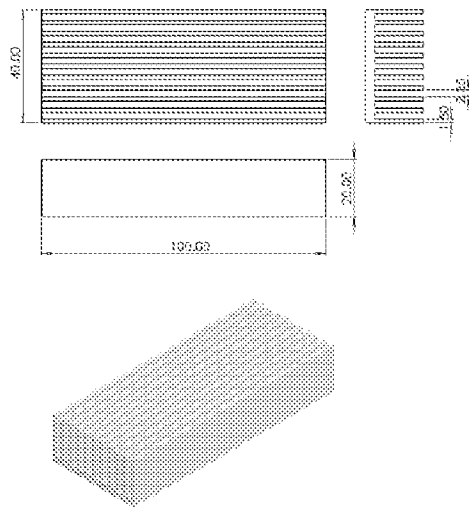


Fig. 11c

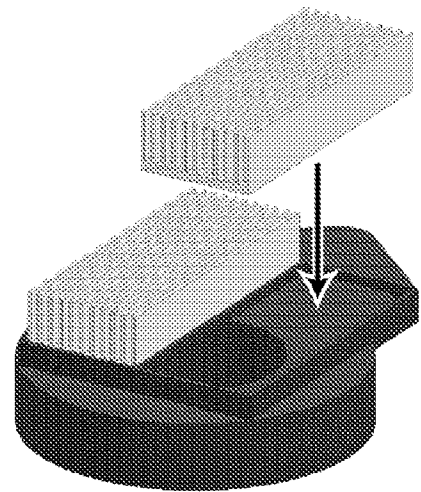


Fig. 12

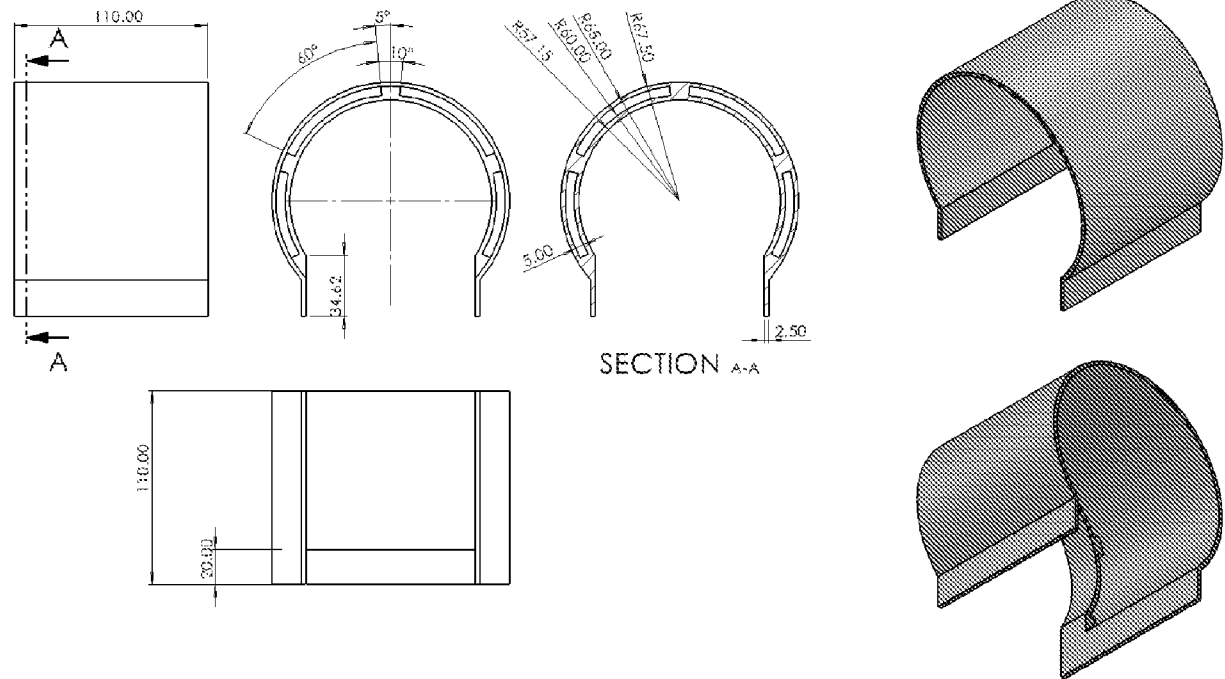


Fig. 13

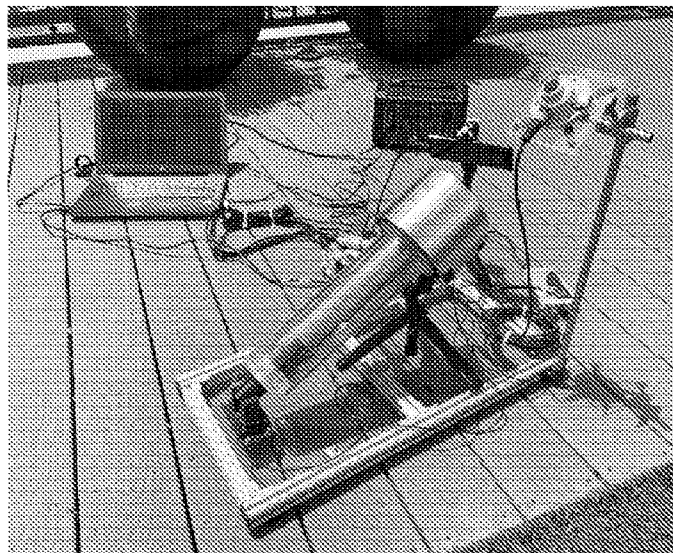
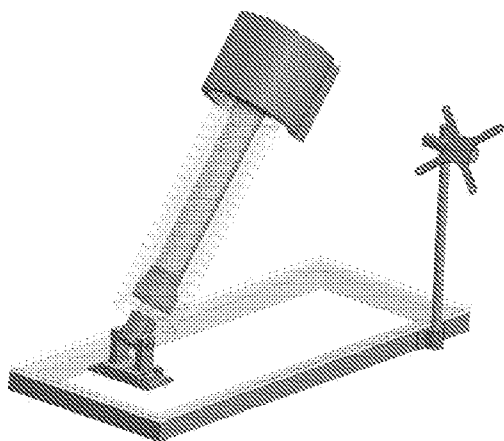


Fig. 14

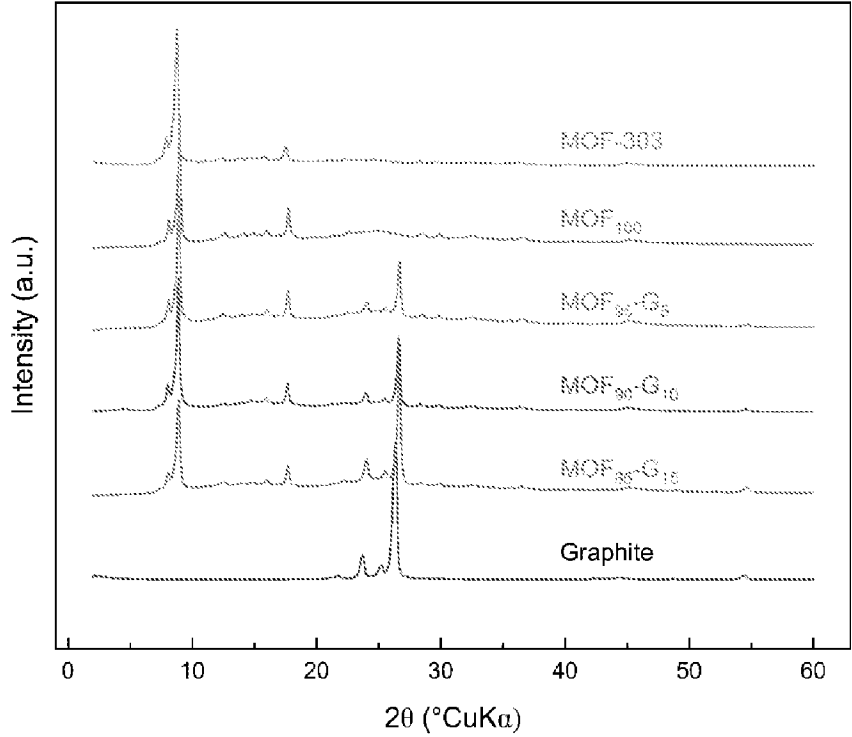


Fig. 15

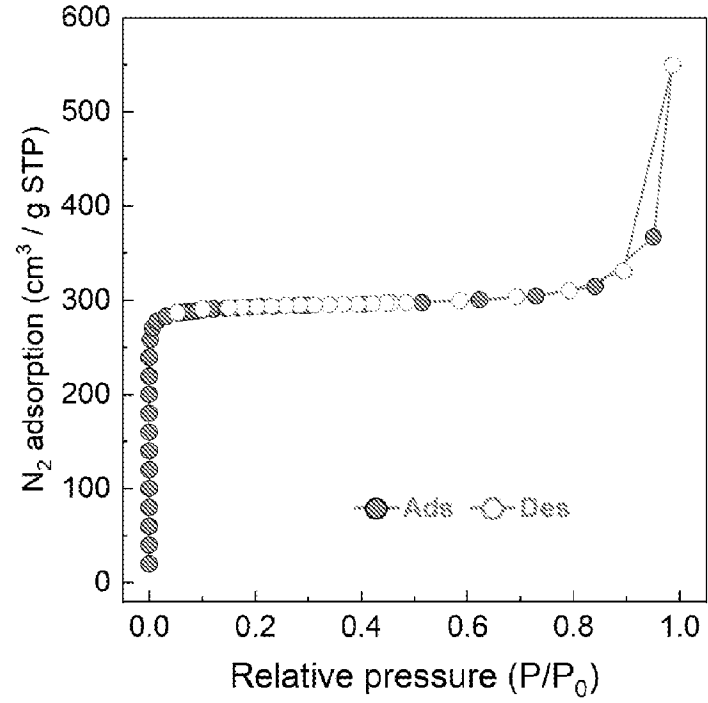


Fig. 16

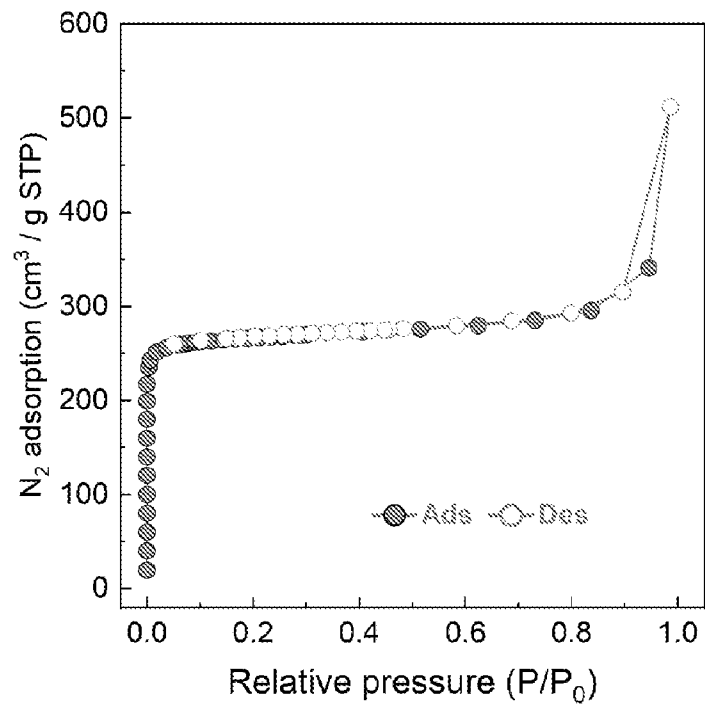


Fig. 17

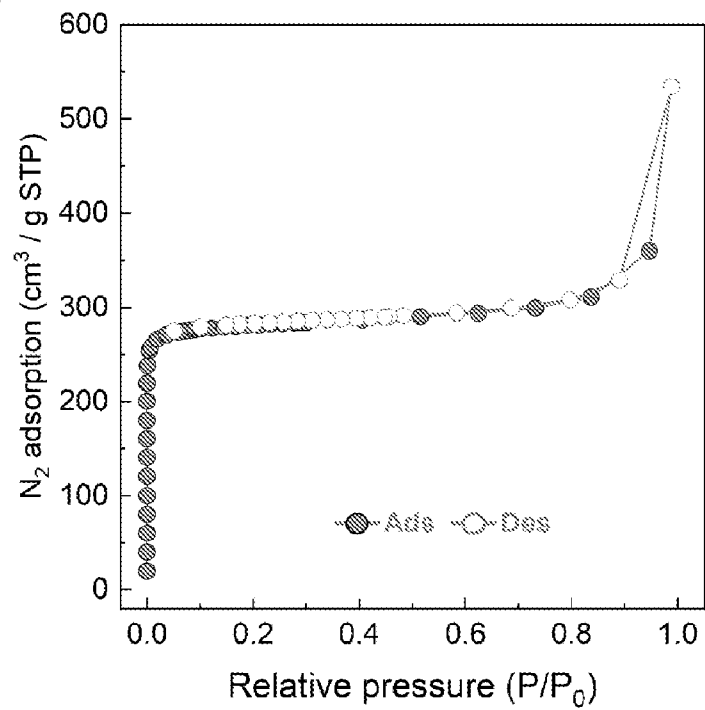


Fig. 18

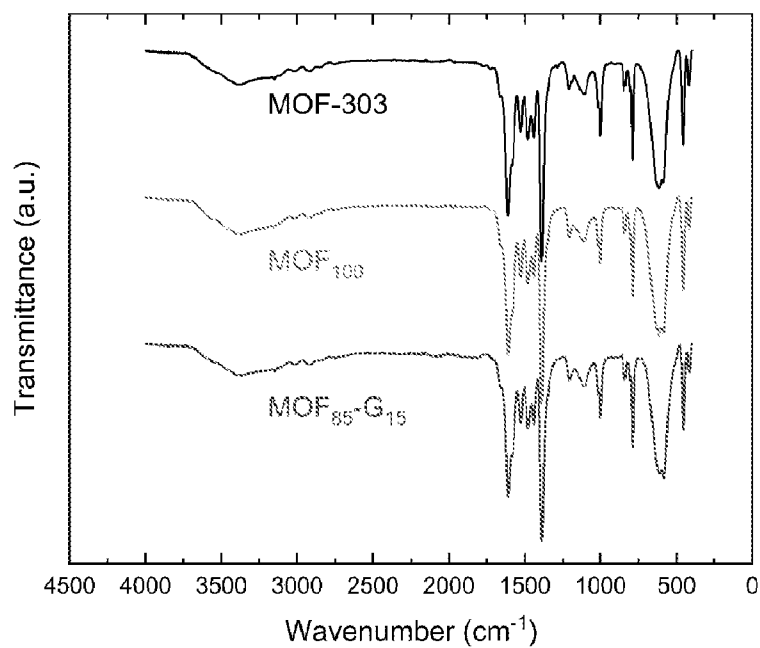


Fig. 19

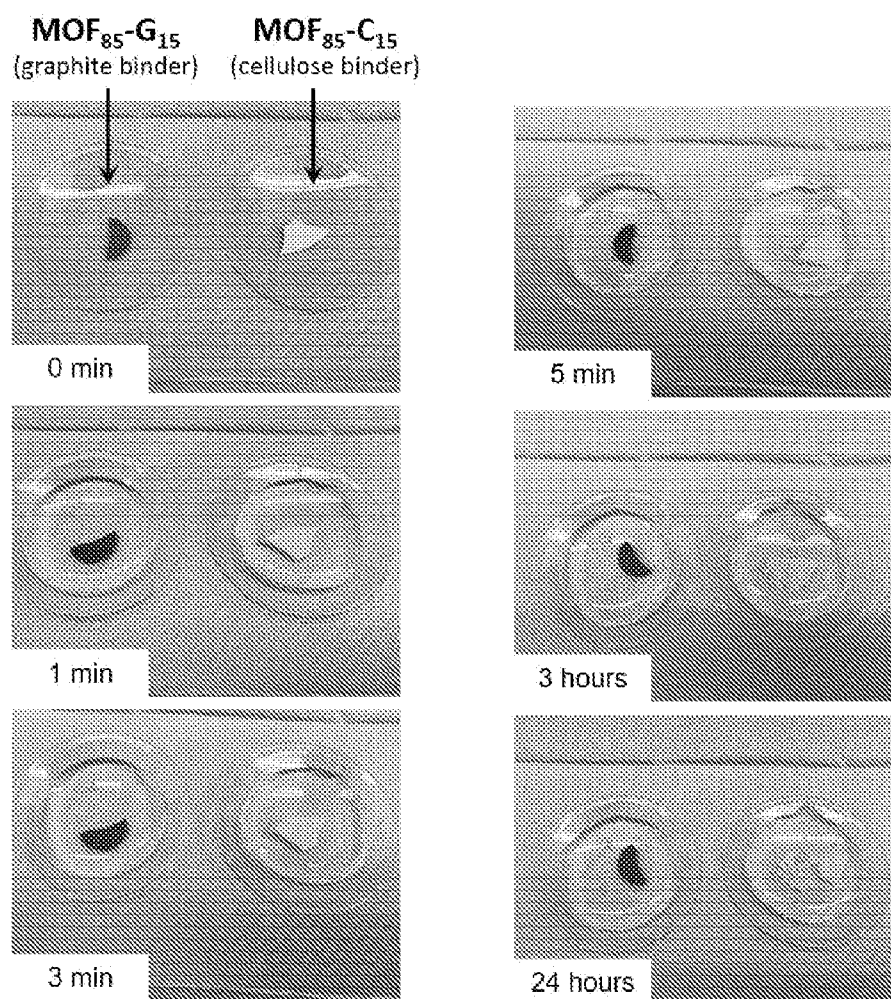


Fig. 20a

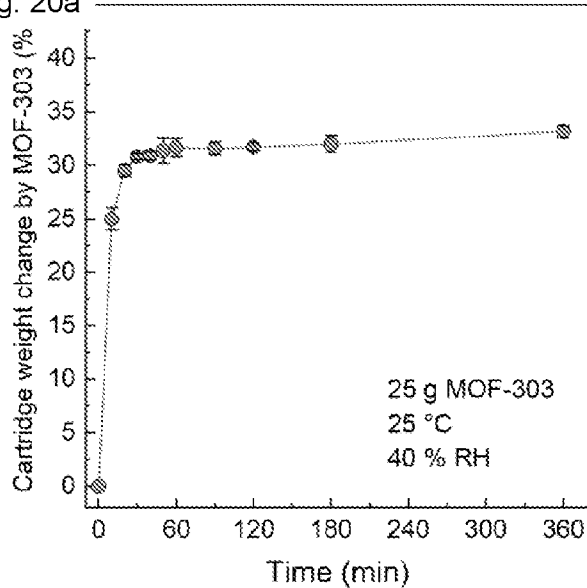


Fig. 20b

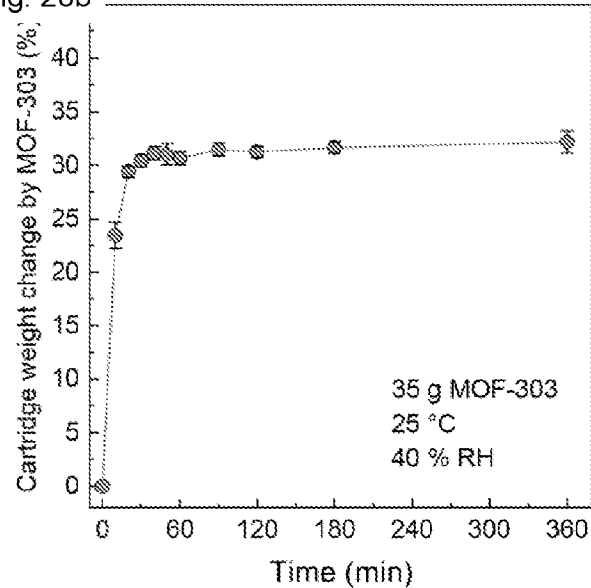
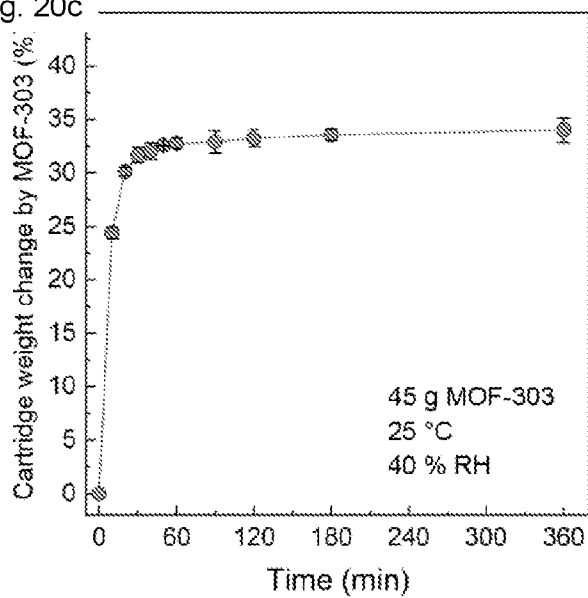


Fig. 20c



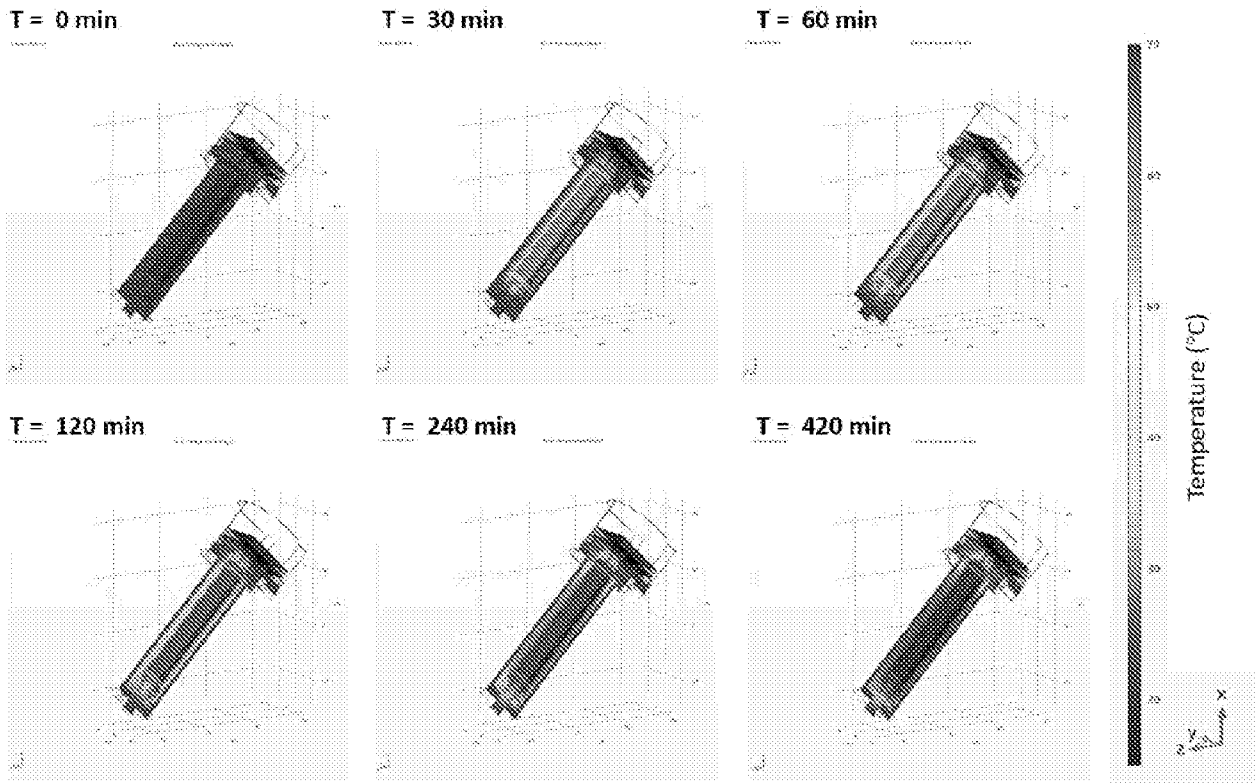


Fig. 21

Fig. 22a

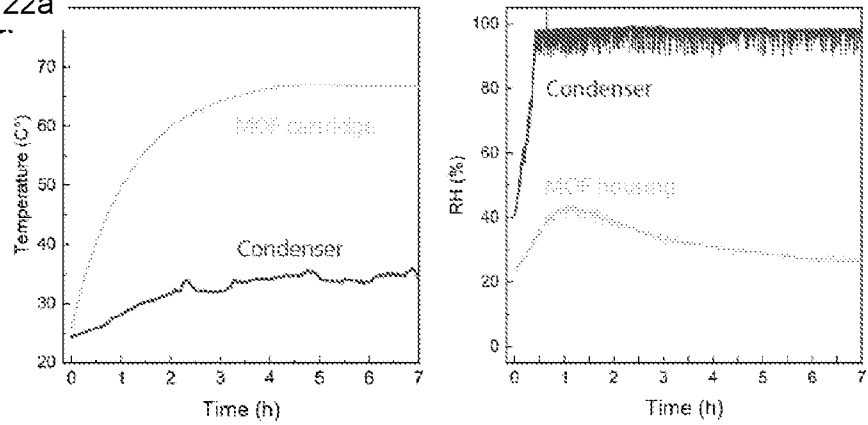


Fig. 22b

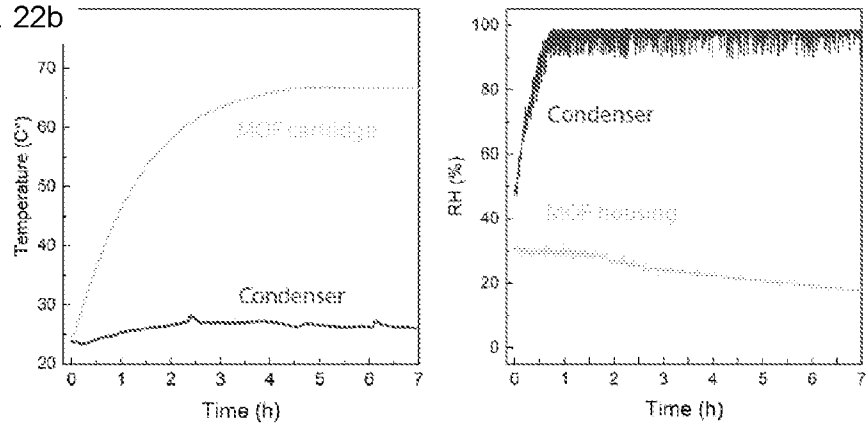


Fig. 22c

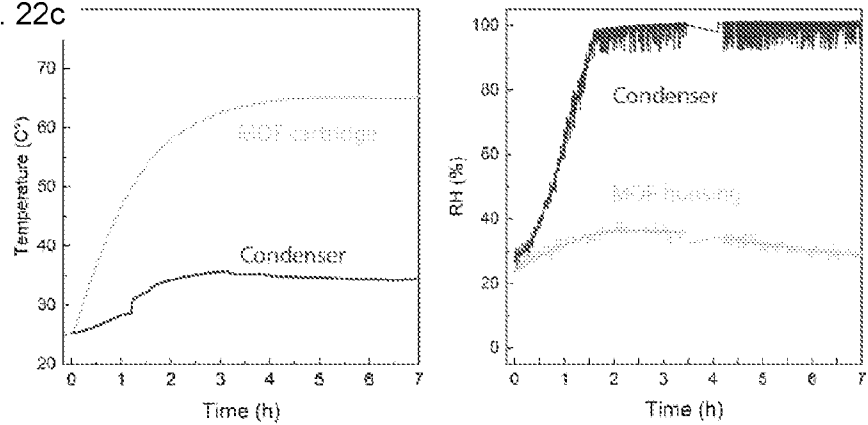
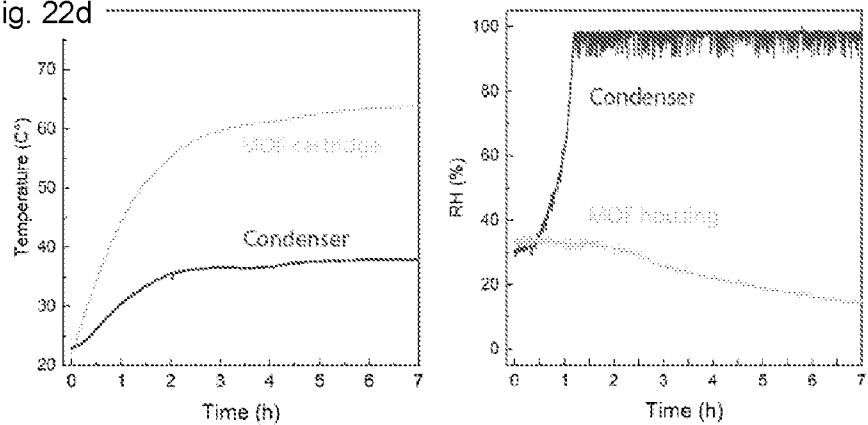


Fig. 22d



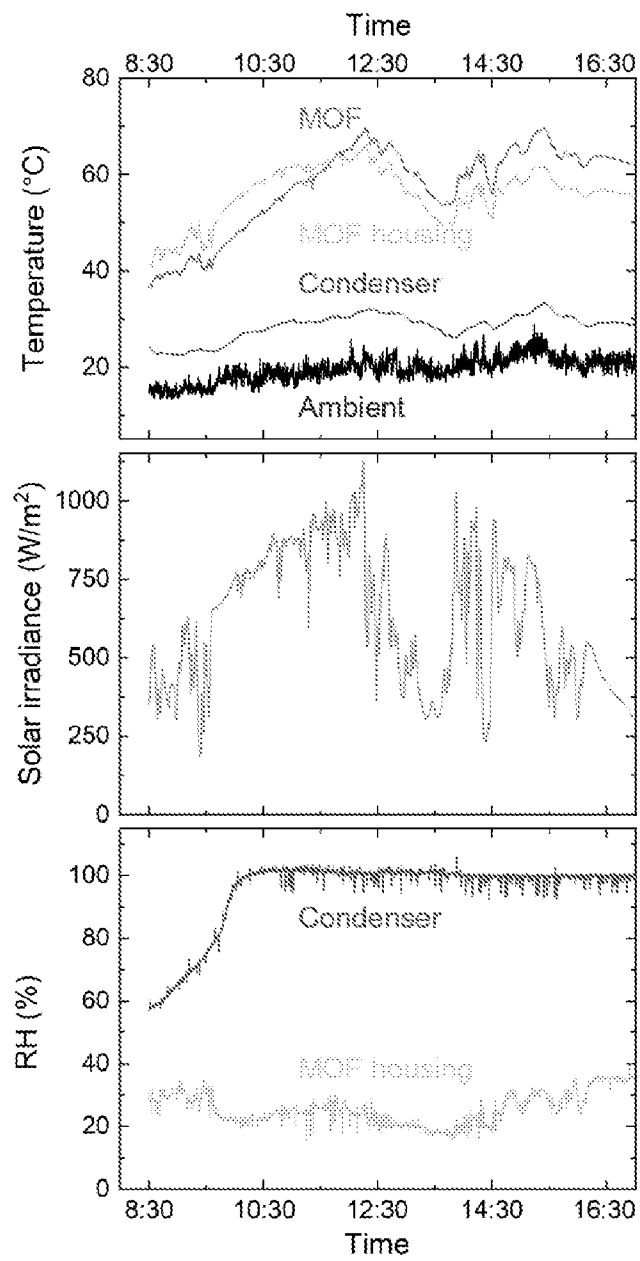


Fig. 23

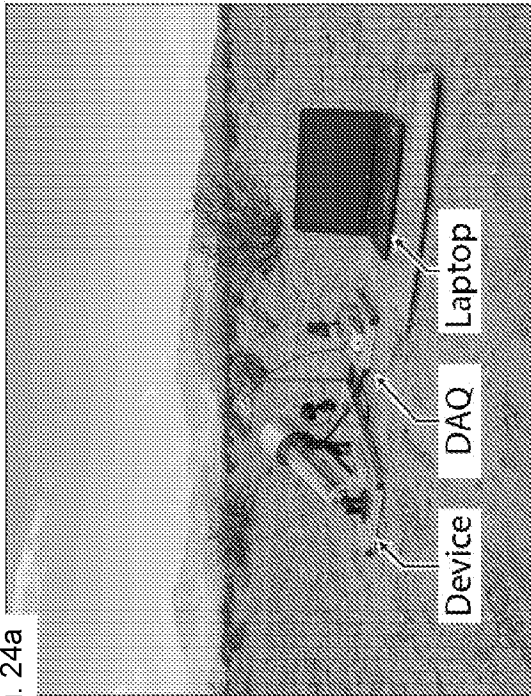


Fig. 24a

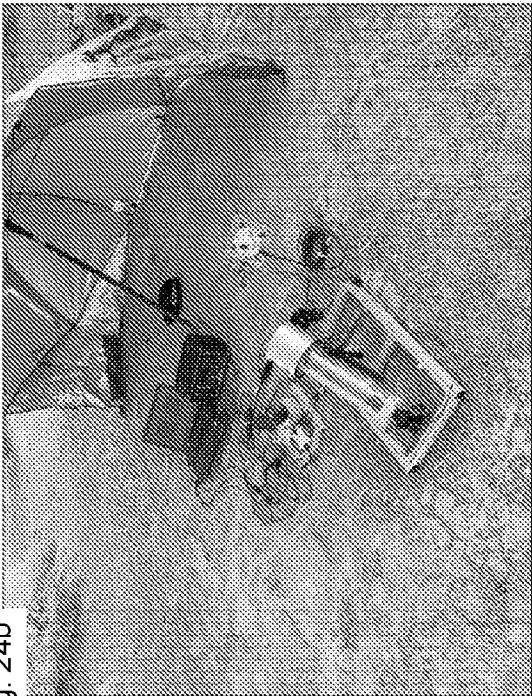


Fig. 24b

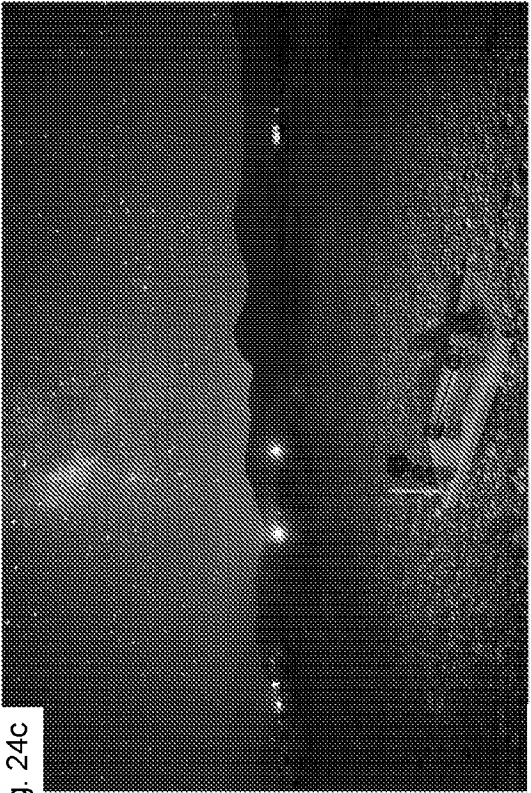


Fig. 24c

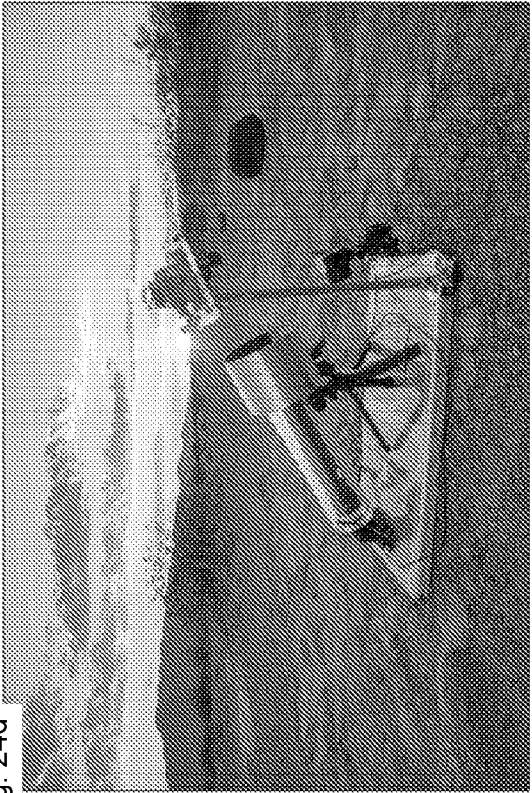


Fig. 24d

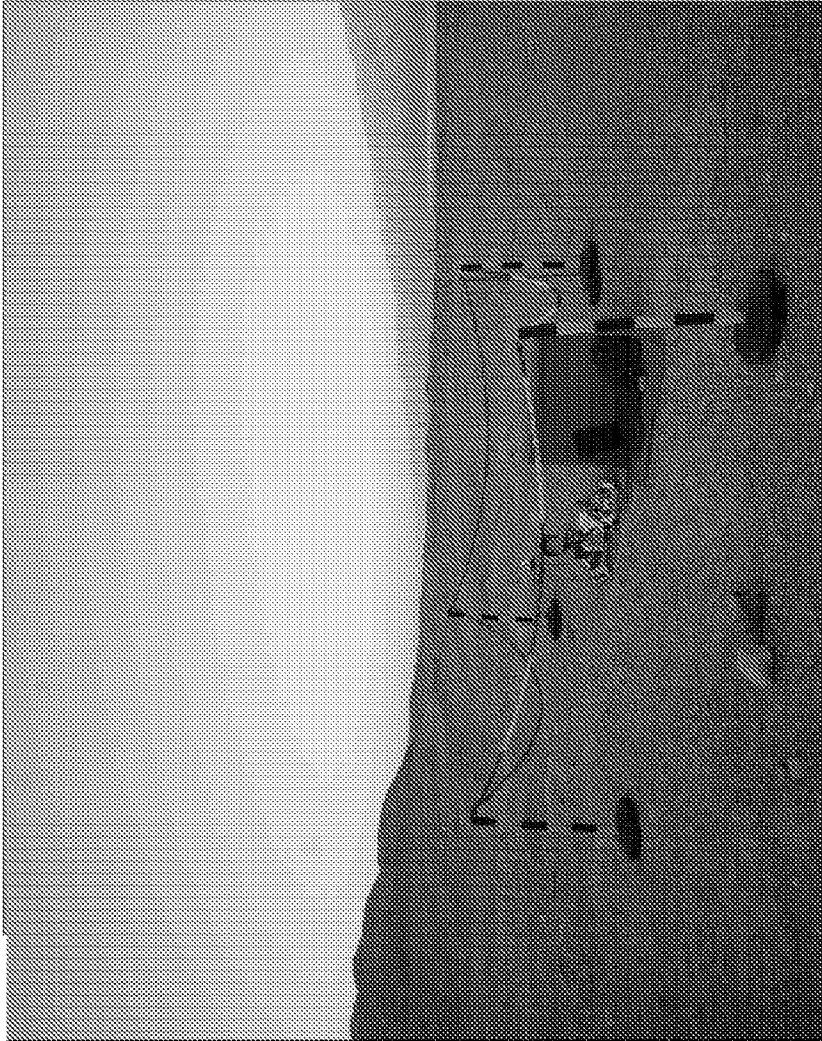


Fig. 25b



Fig. 25a

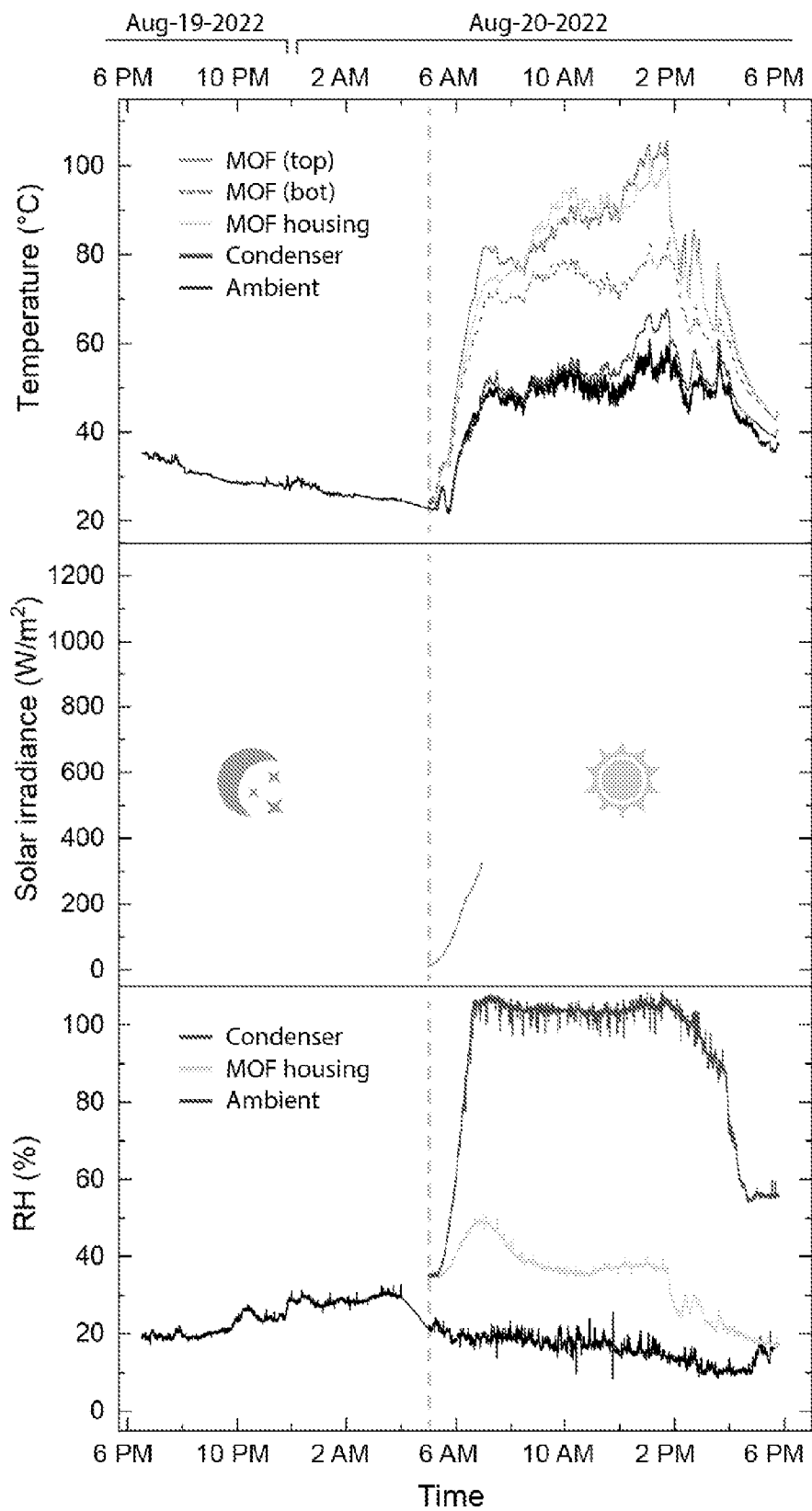


Fig. 26

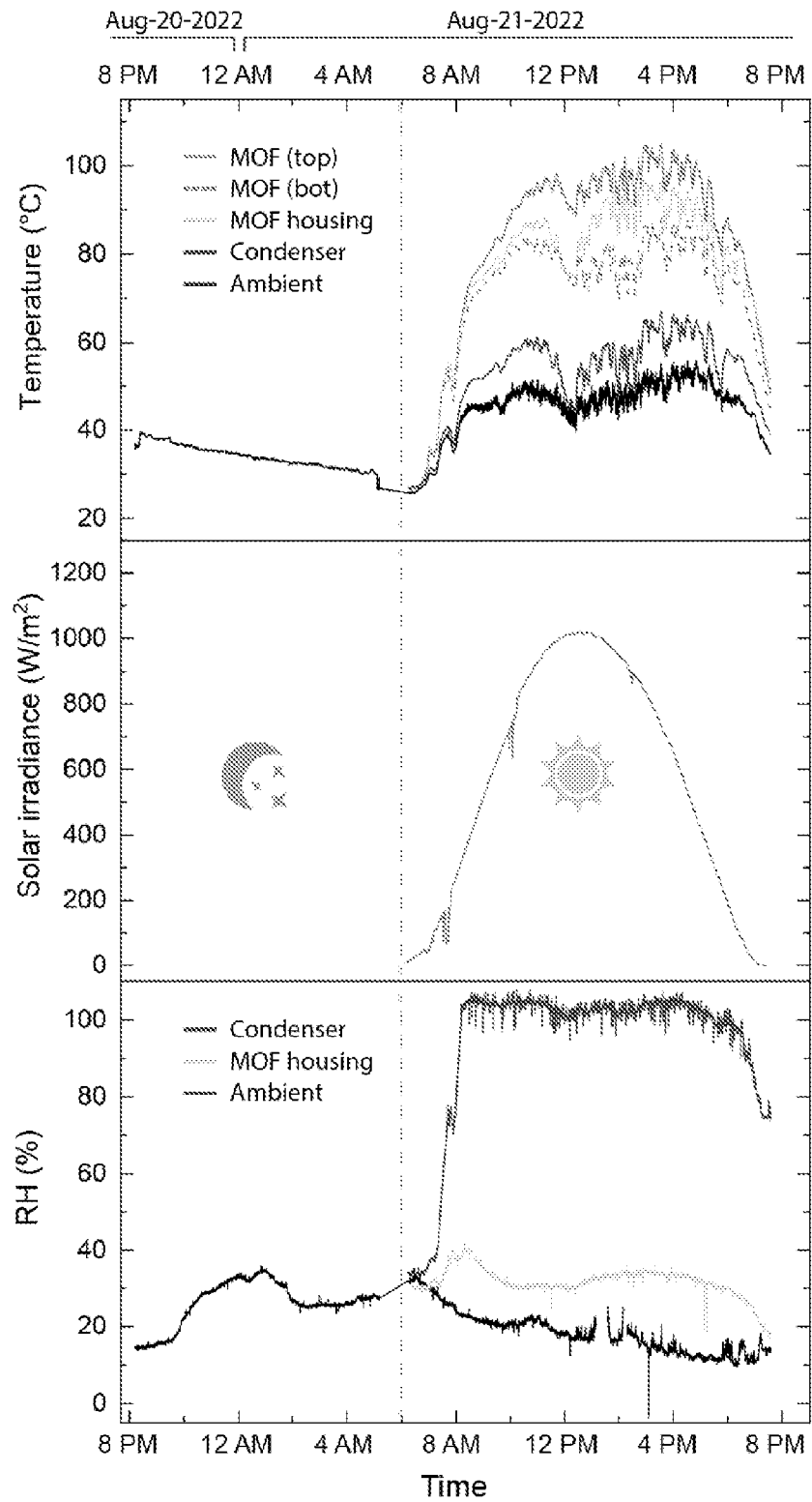


Fig. 27

Fig. 28a

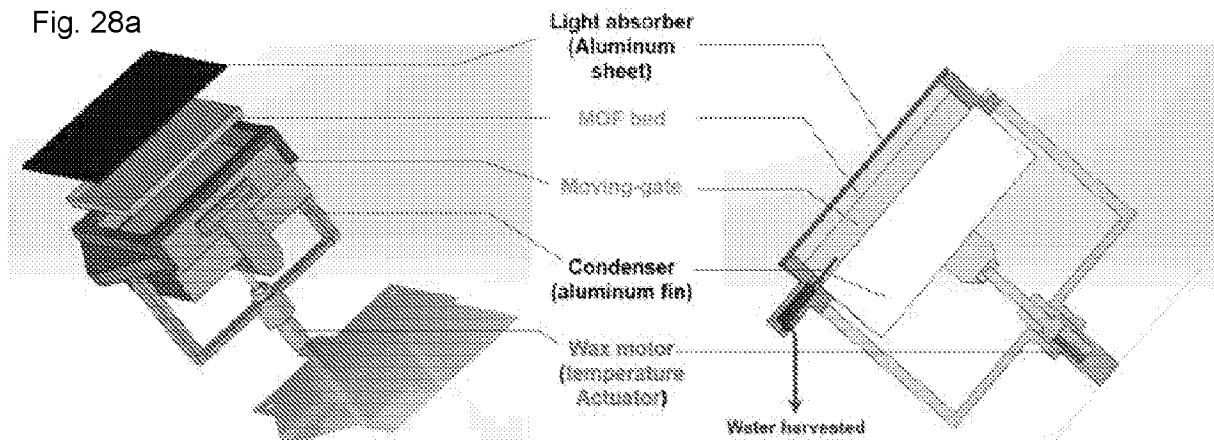
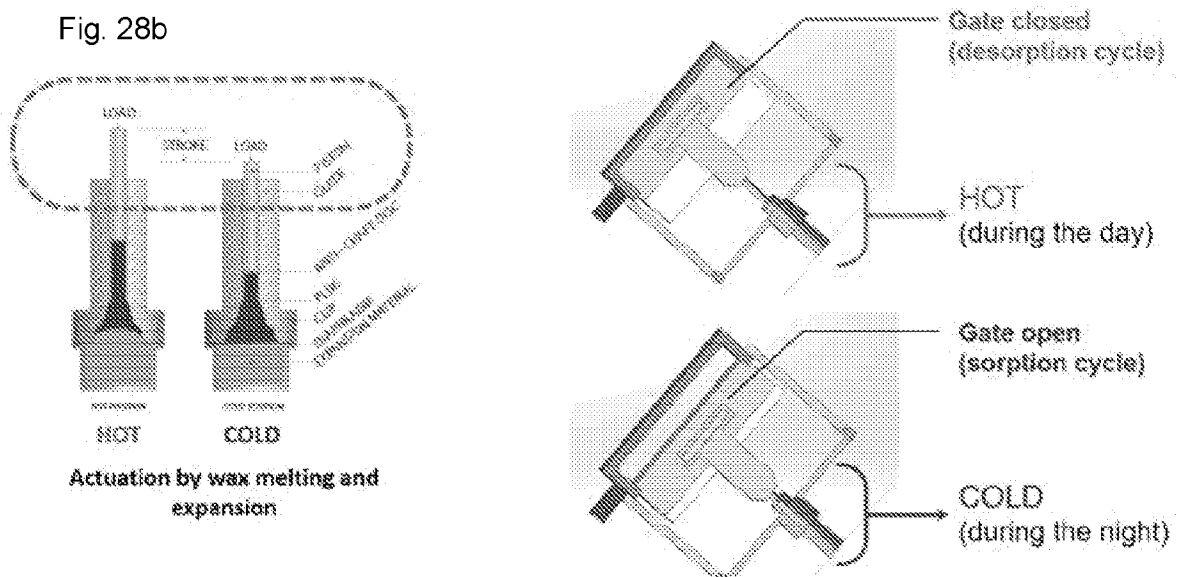


Fig. 28b



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 24/13243

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. B01D 53/26, B01J 20/32, B01J 20/02 (2024.01)

ADD. B01D 15/08 (2024.01)

CPC - INV. B01D 53/26, B01D 53/261, B01J 20/3238, B01J 20/02

ADD. B01D 15/08

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 — A	US 2020/0361965 A1 (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA) 19 November 2020 (19.11.2020)- entire document especially abstract, claim 34, and para [0009], [0139], [0228], [0244]	1-6, 8/5, 11/5-12/5, 26/(1, 5) 7, 8/7, 9, 11/7-12/7, 13-15, 26/7
A	WO 2022/178645 A1 (POLYVALOR, LIMITED PARTNERSHIP) 1 September 2022 (01.09.2022)- entire document	1-9, 11-15, 26
A	WO 2022/013724 A1 (POLITECNICO DI TORINO) 20 January 2022 (20.01.2022)- entire document	1-9, 11-15, 26
A	US 2022/0064913 A1 (MASSACHUSETTS INSTITUTE OF TECHNOLOGY) 3 March 2022 (03.03.2022)- entire document	1-9, 11-15, 26
A	US 2022/0106203 A1 (WATER HARVESTING INC.) 7 April 2022 (07.04.2022)- entire document	1-9, 11-15, 26

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

* Special categories of cited documents:

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

“D” document cited by the applicant in the international application

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

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

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

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

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

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

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

“&” document member of the same patent family

Date of the actual completion of the international search

9 April 2024

Date of mailing of the international search report

MAY 01 2024

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Kari Rodriguez

Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 24/13243

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.: 16-25
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:
Claims 16-25 are referring to Figures where no meaningful opinion could be formed.

3. ☒ Claims Nos.: 10
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.