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A moisture penetrating humidity pump directly powered by one sun illumination

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Summary
The humidity control has a broad and substantial demand all over the industrial, commercial and residential situations. The current humidity pumping technologies require high-intensive maintenance due to the complexity of the mechanical structures. Furthermore, the indirect utilization of solar energy increasing both cost and energy loss. Here, we demonstrate a new humidity pumping concept based on multi-layer moisture permeable panels. Such panels, with a simple structure, may allow the penetration of moisture from indoor(adsorption) to outdoor(desorption) with little heat loss. One sun illumination is introduced as the energy source. A proof-of-concept prototype is designed and established, and successfully dehumidifies the indoor air with a best dehumidification rate of 33.8 g·m⁻²·h⁻¹. By applying such humidity pump, the indoor latent heat load can be handled independently and consumes no electricity. To our scope, this is the first design to realize humidity pumping under one sun illumination without any auxiliary unit.

Keywords: humidity control; humidity pump; moisture penetration; solar energy; photo thermal effect; adsorption and desorption;

Introduction
The ambient humidity collection has become a popular topic due to its important role in water collection and air humidity adjustment, according to their different post-collection management processes. The atmospheric water harvesting, which aims to obtain clean liquid water after the ambient humidity collection, has already been intensively studied.¹⁻³ This contributes significantly to the arid areas with potable water shortage. The humidity control, which focuses on the removal of the water vapor in the air after humidity collection, also attracts dramatic attentions due to the increasing interest on sustainable buildings.⁴⁻⁷ In modern times, nearly 40% of the total energy consumption is associated with buildings worldwide.⁸⁻¹¹ According to the United Nations, 70% of total population or more are trending to live in urban areas by 2050, where the density of buildings is significantly larger than countryside and people usually spend more than 80% of days indoors.¹² This makes the indoor environment control dramatically important and thus increasing attentions have been paid to this field. Evidence shows that more than half of energy consumption in buildings, which is equal to almost 20% of total energy consumption, is resulted from air-conditioning systems.⁹⁻¹¹ Besides, the temperature and humidity management is also critical in many industrial occasions.¹³ As widely acknowledged, roughly 40% of HVAC load is responsible for latent heat load (dehumidification) and the other 60% is for sensible heat load.¹⁴ Thus effective technologies for humidity control would be of great importance. Conventional vapor-compression systems, which is the most preferred dehumidification technology commercially, dehumidify the air through the dew point method, by which the supply air is cooled down to a much lower
temperature than the indoor environment needs while the moisture in the air is condensed and removed\textsuperscript{15}. However, a re-heating of outlet air is essential to satisfy the temperature needs of inhabitants and thus results in extra energy consumption. Previous researches have shown that the temperature and humidity independent control (THIC) system, in which the sensible and latent heat load is regulated separately, has a promising energy saving potential\textsuperscript{15-17}. Therefore, different dehumidification technologies based on ambient humidity collection process have been developed to achieve the expected balance between the energy consumption and indoor thermal comfort. The solid desiccant cooling system may handle the latent heat load independently, and use waste heat or renewable energy, such as solar energy. The refrigerant and desiccant materials involved are mostly environmental friendly. This may result in obvious energy saving potential and positive ecological and economic effects\textsuperscript{18-21} The rotary system, based on solid desiccant system, can handle the latent heat load continuously and more efficiently.\textsuperscript{21} The liquid desiccant absorption system, which utilizes the hygroscopic salt solution instead of solid desiccant, can adjust the indoor humidity accurately and continuously.\textsuperscript{22, 23} In recent years, the Desiccant Coated Heat Exchanger system is developing very fast, with the merits of both vapor compression system and sorption-based system.\textsuperscript{14, 24, 25} The desiccant material is coated on the fins of the heat exchanger so that the latent and sensible heat load can be handled independently and simultaneously. As the concept of sustainable building or zero energy building are receiving increasing impetus, several novel ideas on energy saving technologies in buildings flourished regarding different aspects.\textsuperscript{26-28} Renewable energy resources, in most cases the solar energy, is usually the first choice.\textsuperscript{29} Thus the sorption-based dehumidification technologies becomes very promising choices for building indoor air conditioning.

However, the sorption-based dehumidification technologies are still not that widely applied currently. Some major drawbacks still limit the application in industry and buildings. Due to the adsorption-desorption nature, the working process is usually intermittent.\textsuperscript{19, 21} The installation, especially the rotary system, is often bulky and complex, and this inevitably increases the maintenance cost a lot.\textsuperscript{21} Furthermore, such systems can only utilize the solar thermal energy by introducing additional energy harvesting, energy conversion and energy transportation units and systems, which is also a major reason for bulky and complex installation.\textsuperscript{18} The direct usage of solar energy is attracting attentions currently and large quantities of researches have been carried out regarding the high efficient usage of solar thermal energy in surface localized heating and vapor generation.\textsuperscript{30-33} But unfortunately few researches have been concentrated on the sorption based humidity control technologies which should have a large potential.

In this study, a moisture permeable panel based on solid desiccant directly powered by one-sun illumination is proposed to serve as a passive humidity pump, which can transfer the moisture in the air from indoor to outdoor with a very simple structure. We also report a prove-of-concept prototype that successfully removes the indoor moisture to outdoor using our passive humidity pump only under a one-sun illumination. We introduced both Silica gel(SG) based and SG-MIL101(Cr) based moisture permeable panels for comparison. The MIL-101(Cr) can improve the dehumidification rate and also successfully reduce the relative humidity down to the medium level (around 50%) which fulfills the human thermal comfort requirement.\textsuperscript{34} With such technologies, the indoor latent heat load can be handled independently without consuming electricity and the HVAC systems in buildings are expected to be much more efficient.

### Results

The concept and design of the moisture permeable panel
The moisture permeable panel is consisted of three parts: the porous substrate, the desiccant layer and the photo thermal coating film. The porous substrate is introduced for both holding the desiccants and providing good thermal insulation property. The widely used desiccants such as vermiculite or zeolite powders are inconvenient and difficult to be shape-stable, thus a matrix which may provide skeletons for desiccants to attach is essential. Besides, to prevent the heat loss of the panel, thermal insulation property should be considered. The desiccant layer is responsible for adsorbing water vapor from indoor space, transferring the water molecules from inner surface to outer surface and desorbing the attached water to outdoor space. To achieve such function, a relatively good water capture ability is expected under normal room temperature and humidity, and its desorption should happen under relatively modest temperature. The photo-thermal layer is introduced to provide sufficient desorption heat. Different from the traditional desorption process, the heat is neither coming from hot air which flows over the desiccant layer surface nor from the heat exchanger fins which is coated by desiccant, both of which are energy consuming processes. Instead, the needed heat is directly generated on the desiccant layer surface, which largely simplify the installation of the structure. The photo thermal layer should be made from a material that is very inert and stable considering the variable and even extreme outdoor environment.

**Figure 1.** (a) Schematic structures of moisture permeable panel and expected moisture transfer path. The moisture in the indoor air pass through the porous matrix and is adsorbed by desiccant. The absorbed water molecules pass through the desiccant layer and reach the outdoor surface. The absorbed water is removed by the heat generated by CB powder under sunlight illumination. The panel structure with
In this research, a common thermal insulation foam- the wet foaming phenolic foam (PF) - is introduced as the porous substrate due to its merits of excellent thermal insulation, low-cost and easy shaping etc. Glass fiber and ceramic fiber are also promising alternatives, which are more rigid but suffer from heavier weight and difficult shaping. For the desiccant layer, the silica-gel (SG) and SG-MIL101(Cr) composite material are chosen and investigated. Silica gel is widely applied in adsorption cooling and dehumidification fields due to its advantages of satisfied water capture ability, non-toxic nature, easy fabrication process and low cost.\textsuperscript{35, 36} It plays an important role especially in rotary wheel systems and desiccant coated heat exchanger systems.\textsuperscript{14, 24, 37} The metal-organic-framework(MOF) MIL-101(Cr) has been investigated and applied in several cases such as carbon dioxide capture, hydrogen storage or water adsorption\textsuperscript{38-41}. Here it is chosen as the second candidate since it also enjoys excellent water adsorption ability and stability under extreme weather conditions (hot and strong sunshine).\textsuperscript{42} Besides, it has a type V isotherm according to IUPAC and the S-shape is around medium level(see Figure S1), which is the optimum feature for solid desiccant system. The photo thermal layer is made from carbon black powder with the particle size around 50 nm. These very small size may guarantee the well dispersion of CB powder on the panel surface. By following the ideas above, two kinds of panels, one with pure SG layer and the other with SG-MIL101(Cr) layer, have been proposed and fabricated, as shown in Figure 1b and 1c. A cross section photo of a real panel sample is shown in Figure 1d for better understanding. Detailed fabrication process is shown in Experiments and Methods. It should also be noted that two structures of desiccant layer are applied, either condensed or loose, according to the amount of desiccant in the layer. Details for each panel is listed in supplementary information Table S1.

**Different desiccant layer structures with different mass transfer abilities**

The SEM and TEM pictures of panels are first given to understand the panel surface morphology (Figure 2). Figure 2a clearly shows the pure PF surface structure. The pores around the skeletons are more than 100 μm, which provide enough space for both desiccant adhesion and moisture transport. In the condensed layer (b), most of the pores are filled with SG and this is expected to result in a larger adsorption quantity. On the contrary, the loose layer (Figure 2c) spares more pores so that more channels can be involved in mass transfer instead of being blocked pores. But the influence of less adsorption amount should be further evaluated. Figure 2d gives the details of SG-MIL101(Cr) composite desiccant. Very small MIL101(Cr) crystals is observed to be aggregated on the SG surface (and also inside the SG bulk). The TEM pictures provides clear appearance of the MIL101(Cr) crystals (Figure 2e and 2f). The dimension of single MIL101(Cr) crystal is around a few hundred nm and very regular pore and channel structures can be seen in Figure 2f. The dynamic water adsorption as well as the nitrogen adsorption of the MIL101(Cr) involved are shown in supplementary information, Figure S2.

To acquire the specific evidence on mass transfer, the Water Vapor Transmission (WVT) test was carried out. The experimental details are shown in Experiments and Methods section. The mass loss of each kind of panels were weighed and showed in Figure 2g, on which the slope of the line indicates the mass decrease rate proportion to WVT ability. The reference (black square) curve represents the pure PF foam sample while red dots, blue and green triangles stand for panels with loose SG layer, condensed SG layer and loose SG-MIL101(Cr) composite layer, respectively. All the mass loss curves show a linear shape. It is obvious that the impregnation of SG into the PF foam diminishes the moisture transmission ability, and the more SG there exists, the worse the
mass transfer rate is. The addition of MIL-101(Cr) hardly influence the WVT ability and the two lines of SG loose layer and SG-MIL-101(Cr) layer are mostly identical. This is attributed to the tiny particle size and very small aggregation domains of MIL-101(Cr). As presented in Figure 2d, the aggregated domains are in the range of lower than 1 μm and the particles are even much smaller, which can be considered as a thin film covering the SG surface. These MOF particles and aggregated domains barely change the pore and channel structures, and thus consequently influence very little on the WVT ability. This result corresponds to our suggestion above that the amount of accessible channels and pores in the desiccant layer are considered as the dominating reasons.

Quantitatively, the specific indicators, WVT, water permeance and permeability can be expressed by the following equations according to the Standard Test Methods for Water Vapor Transmission of Materials:

\[ WVT = \frac{G}{tA} \]  
(1)

where \( G \) stands for the total mass decrease amount (in gram), \( t \) the time (in hour), \( A \) the area of the sample mouth (in \( m^2 \)).

\[ \text{permeance} = \frac{WVT}{\Delta p} = WVT/S(R_1 - R_2) \]  
(2)

where \( \Delta p \) indicates the vapor pressure difference between two sides of the tested samples, \( S \) the saturation vapor pressure under test temperature, \( R_1 \) and \( R_2 \) the relative humidity between two sides of the tested samples.

average permeability = permeance \times thickness \]  
(3)

The sample mouth area is 9 cm\(^2\) (3cm \( \times \) 3cm) and the test environment is carefully controlled at 23℃, 50% RH. Thickness of all the samples are identical. Using the equations introduced above, the WVT and water permeance of each sample is calculated. The detailed results are listed in Table 1. Basically, the WVT and permeance of panels with loose SG layer are 1.5 times higher than those of panels with condensed SG layer, and are almost identical to those of panels with SG-MIL101(Cr) composite desiccant layer. So it is very obvious that both loose SG layer and loose SG-MIL101(Cr) composite layer have good mass transfer abilities while that of the condensed layer is much worse.

**Table 1.** The mass loss rate, WVT, permeance and permeability of moisture permeable panels with different desiccant layer structures.

| Desiccant layer structures | Mass loss rate (g·h\(^{-1}\)) | WVT (g·h\(^{-1}·m^2\)) | Permeance (g·h\(^{-1}·m^2·pa^1\)) | Permeability (g·h\(^{-1}·m^1·pa^1\)) |
|----------------------------|-------------------------------|------------------------|---------------------------------|----------------------------------|
| SG Condensed               | 0.0400                        | 44.4                   | 0.0226                          | 1.13 \times 10^{-4}              |
| SG Loose                   | 0.0598                        | 66.4                   | 0.0338                          | 1.69 \times 10^{-4}              |
| SG-MIL-101(Cr)             | 0.0584                        | 64.8                   | 0.0330                          | 1.65 \times 10^{-4}              |
Figure 2. SEM images of (a) pure wet-foaming phenolic foam surface, (b) PF foam with condensed SG layer, (c) PF foam with loose SG layer, (d) MIL-101(Cr) aggregates on the SG particle surface; TEM images of (e) pure MIL-101(Cr) crystals and (f) the zoomed-in area of dashed square in (e). Results of permeability test (g). The reference sample in permeability test stands for the pure wet-foaming phenolic foam without any silica-gel attachment.
Figure 3. Infrared(IR) images of different panels under one-sun illumination after a fixed time. (a) wet panel with SG layer, surface without CB coating; (b) wet panel with SG layer, surface with CB coating; (c) wet panel with MIL101-SG layer, surface with CB coating; (d) dry panel with SG layer, surface with CB coating.

The surface temperature (regeneration temperature) enhancement by the carbon black (CB) photo thermal layer

The Infrared (IR) images were taken to evaluate the photo-thermal effect induced by the CB coating, as shown in Figure 3. Four samples with different structures were placed under the same light source with 1000W/m² intensity. Details of each sample is listed in Table 2. Photos were taken after 0 minute, 5 minutes and the 30 minutes and all the samples (except sample d) reached equilibrium at 25°C, 70% RH working condition before they are put under illumination. A relatively small temperature rise of sample a (average temperature: 37.7°C after 5 minutes) is observed while the sample b has a much faster temperature increase (average temperature: 56.7°C after 5 minutes). This can be ascribed to the CB coating on the surface which generates much more heat due to the photo thermal effect. The sample d, which has the identical structure to sample b, is pre-dried before photo taking and thus resulted in an even higher surface temperature (average
temperature: 58.4°C after 5 minutes) since water desorption usually consumes a certain amount of heat. The sample c, which has a SG-MIL101(Cr) composite desiccant layer, has a lower temperature distribution (average temperature: 47.0°C after 5 minutes). The dominating reason is believed to be the larger water capacity of the composite desiccant and faster water losing rate. More detailed information can be seen in supplementary information, Table S2. The IR images clearly prove that the CB coating can largely increase the surface temperature. Besides, the desorption can happen under one-sun illumination condition according to the lower temperature of sample b and c, and obviously the composite desiccant desorbs water faster than the pure SG (also see supplementary information, Figure S2).

Table 2. Details of each sample in IR images.

| Sample | a | b | c | d |
|--------|---|---|---|---|
| Desiccant | SG | SG | SG-MIL101(Cr) | SG |
| CB coating | No | Yes | Yes | Yes |
| Dry or wet | Wet | Wet | Wet | Dry |

**Proof-of-concept prototype and dehumidification results**

To demonstrate the feasibility and to evaluate the performance of this novel moisture pump under real working condition, a proof-of-concept prototype applying the MP panel was established and tested. A scaled down model of a house was made with the dimension of 70cm * 40cm * 40cm. Figure 4a gives the sketch of this prototype. Two windows with an area of 5cm * 5cm were design for MP panel installation. Movable outer shields and inner shields were introduced for shielding the sunlight or the indoor air depending on different working processes. By opening the inner shield of one MP panel, this panel is absorbing water vapor from indoor air while the outer shield is closed, keeping this panel from sunlight illumination. Meanwhile, the inner shield of the other panel is closed while the outer shield is opened, isolating this second panel from indoor air but under illumination from sunlight, as shown in Figure 4b. After a certain period, the shields are switched and the panel working condition is reversed. The first panel which has absorbed a certain quantity of water is now exposed to sunlight while the other panel which has been regenerated well is now capturing the water vapor from indoor space, as shown in Figure 4c. By switching the working mode alternatively in a controlled period, this system is absorbing indoor water vapor and losing water to outdoor simultaneously.

Two identical MP panels with 5cm*5cm area was installed in each window. The initial working condition inside the box was 25°C, 65% RH and both panels reach equilibrium under such working condition. The box was tightly sealed to prevent any possible leakage and one panel with inner shield closed was exposed to one-sun illumination (1,000W·m⁻²) while the other panel was still covered by outer shield. The switch time period was chosen as 20 minutes. After the switch, the working mode of each panel was changed and this switch repeated within the whole dehumidification process. The outside working condition was kept constant at 25°C, 70% throughout the whole experiment. Figure 4d presents the results of this prototype applying panels with both SG loose layer (open cycles) and SG-MIL-101(Cr) layer (closed cycles) and several consecutive cycles of each panel were chosen and presented. For SG loose layer panel, obvious drop of relative humidity (open cycle, blue) as well as water content (open cycle, black) appeared in the early periods, indicating the adsorption of water vapor by the desiccant layer in the panel and the decrease of the relative humidity of the indoor space. But as the setup kept working and the RH went down (around 60%), the RH drop became more and more subtle and finally reached a near constant state. The indoor temperature remained almost constant and only very small
temperature variation was observed (less than 0.3°C) resulted from adsorption heat. This is associated with the thermal insulation layer since most of the adsorption heat generated in the desiccant layer spread through the desiccant layer rather than the porous thermal insulation layer, leaving the inside temperature almost unchanged. The specific dehumidification rate can be calculated as follows:

\[
r = \frac{\Delta m}{t \cdot S} \text{(g·m}^{-2}·\text{h}^{-1})
\]

where \(\Delta m\) (g) stands for the water loss during the whole dehumidification process, \(t\) represents time (h) and \(S\) stands for the total area of the MP panels (m\(^2\))

\[
m = d \cdot m_{\text{air}} = d \cdot V \cdot \rho \text{(g)}
\]

\[
d = 0.622 \frac{R_{\text{H}} \cdot P_s}{B - R_{\text{H}} \cdot P_s} \text{(g·kg}^{-1})
\]

where \(d\) is the water content (g/kg) of the air, \(V\) is the volume of the model house, \(\rho\) is the density of air at the working temperature, \(R_H\) is the relative humidity (%), \(P_s\) is the saturated water vapor pressure at the working temperature, \(B\) stands for the atmospheric pressure.

For the panel with SG layer, only the first 3 cycles were taken into consideration. The indoor relative humidity dropped from 65.0% to 62.2% and the water content correspondently varied from 12.74 g·kg\(^{-1}\) to 12.29 g·kg\(^{-1}\), resulting in an average dehumidification rate of \(r=24.2\) g·m\(^2\)·h\(^{-1}\).

For the panel with SG-MIL101(Cr) layer (closed cycles), the performance was much better. During the first 3 cycles, the RH dropped obviously faster than the SG layer panel did. When the RH (closed cycles, blue) reached around 60%, the drop rate decreased to a moderate level but still kept going down regardless of this low RH condition. The following several cycles clearly showed that the RH kept going down to a much lower value. Furthermore, Figure 4e presents a few cycles of SG-MIL101Cr panel working under much lower RH condition (around 52%, the medium RH level). Under such working condition, the indoor RH can still be steadily decreased. This is the major difference between SG-MIL101Cr layer and the SG layer. It is evident that the SG lost the dehumidification ability under such indoor-outdoor working conditions. But the MIL101Cr can still have a satisfied water adsorption ability under the same condition, as described above in the Concept section. Below 60% RH, what contributes to the RH drop is only the MIL101Cr rather than SG.

To evaluate the dehumidification rate quantitatively, the process should be divided into two regions: the high RH region (higher than 60%) and the low RH region (lower than 60%). At high RH region, the water content dropped from 12.76 g·kg\(^{-1}\) to 12.13 g·kg\(^{-1}\) with an average dehumidification rate of \(r=33.8\) g·m\(^2\)·h\(^{-1}\). At low RH region, the water content decreased from 12.13 g·kg\(^{-1}\) to 11.59 g·kg\(^{-1}\) with an average dehumidification rate of \(r=15.1\) g·m\(^2\)·h\(^{-1}\).
Figure 4. Illustration of proof-of-concept prototype for moisture permeable panel performance evaluation. (a) the setup of scaled down model. (b) and (c) present the working process. The panel under sunlight illumination is losing water while the one shielded from sunlight is adsorbing water vapor from indoor air. System performance of different panels(d): panels with loose SG layer (open cycles) and panels with SG-MIL101(Cr) layer (closed cycles). The red, blue and black symbols represent the temperature (°C), relative humidity (%) and water content of the air(g/kg), respectively. Vertical dashed lines indicate the switching time period (20 minutes). (e) the system performance of SG-MIL101(Cr)
panel close to medium RH level (around 50%). The red, blue and black symbols represent the temperature (°C), relative humidity (%) and water content of the air (g/kg), respectively.

The adsorption-desorption cycle test was carried out to better understand the difference between SG panel and SG-MIL101Cr panel. The adsorption processes were carried out at different conditions: 25°C-70%RH and 25°C-50%RH while the desorption processes were taken under one constant working condition: 25°C-70%RH (The desorption only takes place on the outside surface, where the environment condition is considered as constant). The mass difference of each cycle represents the water transportation ability of each sample under certain conditions. The adsorption and desorption were carried out alternatively using different setups (Figure 5a, b) with a period of 20 minutes. During this process, the mass change of each sample was measured and recorded. Six stable cycles were chosen and shown in Figure 5, (c) to (f). The squares stand for SG panels while the cycles represent SG-MIL101Cr panels. Under 25°C, 70%RH, both SG (c) and SG-MIL101Cr (d) panels have satisfied mass differences, 0.07g and 0.084g, respectively, which equal to the effective amount of water transported per cycle. The better performance of the composite panel may result from the larger water uptake ability of MIL101Cr. Under 25°C, 50%RH, however, the mass differences of both samples decreased a lot, especially for SG panel(e). Roughly 0.005g per cycle is observed. The mass difference of SG-MIL101Cr sample (f), although decreases, still remain at a moderate value of 0.4g. It is very clear that under such medium RH condition as well as the photo thermal driven condition on the outside surface, the SG panel lose most of the water capture ability since the difference of water uptake amount between the indoor and outdoor working condition is too small to provide enough positive moisture potential as the mass transfer driven force. On the other hand, MIL101Cr can still keep an adsorption-desorption cycle with obvious water uptake amount according to its isotherms. Therefore, it is evident that the SG-MIL101Cr panel not only performs better in the high RH region, but can successfully reduce the indoor RH down to medium RH level as well.
Figure 5. The adsorption-desorption cycles. The experimental setup of adsorption (a) and desorption (b) processes are shown. Two different working conditions are chosen for adsorption process while only one constant working condition is applied for desorption. The mass differences of the cycles of SG panel at 25°C, 70%RH (c) and 25°C, 50%RH (e), SG-MIL101Cr panel at 25°C, 70%RH (d) and 25°C, 50%RH (f) are shown.

Discussion

Estimation of latent-sensible heat load conversion

The introduction of this solar humidity pump may realize the independent control of temperature and humidity. Usually when certain amount of moisture is adsorbed by solid desiccant, the corresponding amount of latent heat is conversed into sensible in the form of adsorption heat. If handled improperly, most of this heat may increase the overall indoor heat load and diminish the energy conservation introduced by this solar humidity pump. A detailed mathematic modeling is beyond the scope of this paper, but a brief estimation is necessary and enough to demonstrate the idea of structure design. As the dynamic adsorption curve shows (Figure S2), the porous PF layer may influence the overall WVT ability of the panel. But the PF has such an excellent thermal insulation property that it may greatly weaken the heat loss of the panel, and therefore the little
influence on mass transfer can be neglected. If the desiccant layer is in direct contact with the indoor air (Figure 6a), the heat flux to indoor \(Q_{in}\) and outdoor \(Q_{out}\) can be expressed as:

\[
Q_{in} = h \cdot A \cdot \Delta t \\
Q_{out} = \frac{\lambda_{SG}}{\delta_{SG}} \cdot A \cdot \Delta t
\]  

(7) \hspace{1cm} (8)

For simplicity, we consider a simple natural convection condition, where the \(h\) is around 10 W/m\(^2\)K; The thermal conductivity of the SG layer is around 0.1 W/mK and the sample thickness 1 cm, thus the value of \(\frac{\lambda_{SG}}{\delta_{SG}}\) is also around 10 W/m\(^2\)K. So under such condition, the \(Q_{in}\) roughly equals \(Q_{out}\). In comparison, by introducing the multilayer structure, the water vapor should first go through the porous PF layer before it reaches the SG layer interface. Similarly, the adsorption heat transfer path \(Q'_{in}\) and \(Q'_{out}\) can be written as:

\[
Q'_{in} = \frac{\lambda_{PF}}{\delta_{PF}} \cdot A \cdot \Delta t \\
Q'_{out} = \frac{\lambda_{SG}}{\delta_{SG}} \cdot A \cdot \Delta t
\]  

(9) \hspace{1cm} (10)

The thermal conductivity of pure PF layer is only around 0.03 W/mK, and in this research the thickness of PF matrix layer is identical to that of SG layer. Therefore, the value of \(\frac{\lambda_{PF}}{\delta_{PF}}\) is around 3 W/m\(^2\)K. Under such condition, the value of \(Q'_{in}\) equals 30% of \(Q'_{out}\). Furthermore, the thickness of the PF layer \(\delta_{PF}\) can be much larger than it was in this research and consequently lead to a much smaller \(Q'_{out}\) value and \(Q'_{in}:Q'_{out}\) ratio.

**Figure 6**, Schematic diagram of heat transfer in adsorption process. (a) Panel without a porous matrix layer inside. Most of the heat is transferred to indoor air via convection; (b) Panel with a porous matrix layer. Most of the heat is transferred to outdoor space.

**Potential applications**

A bright future for a broad application of such moisture pump is expected. Potential application situations may include commercial and residential buildings, industrial plants, and electronic devices etc. Such moisture pump can be easily integrated with construction materials so that a moisture permeable wall or window is expected. Thus the indoor latent heat load can be independently handled by this humidity pump in the daytime, resulting in a higher efficiency of
the cooling unit which could only deal with the sensible heat load. Similar construction structures can be expected in industrial plants, but with much larger scale. Another application situation is the humidity control inside some precise electronic devices. The moisture often appears as a disaster inside the precise electronic devices, which may disable the current circuit or even destroy the whole device. A common approach to remove the moisture inside the device can be achieved by drying with hot wind, but this requires the unsealing of the device which may bring in other impurities or damage the mechanical parts during disassembly or assembly. By applying such micro-scale humidity pump, the moisture removal process is available without the need to disassemble the device, leaving no risk of further damage or impurity introduction. Under such circumstances, the heat source is no longer limited as sunlight, but could be any kind of surface heating technology.

**Limitations of the Study**

The sun illumination condition applied in the experiment is idealized. This research is a new concept proposal and validation rather than a systematic study of such humidity pump system. Therefore, the sun illumination condition is simplified in order to better understand the working process. However, under real conditions, the solar radiation usually grazes the building façade rather than incident perpendicularly, thus solar radiation model should be then considered to better evaluate the working performance under real conditions. Such work should be carried out in a more systematic investigation of such humidity pump system, which includes the performance tests of some standard working conditions.

Besides, this humidity pump still suffers from a relatively low dehumidification rate compared with both vapor compression system and conventional solid desiccant cooling system. The relatively poor water vapor transfer ability is the dominant reason. The key to improve this issue very largely lies both on the material science which may provide more appropriate candidate desiccants and structure design that could optimize the facility with aligned channels and good thermal insulation, if possible. The material fabrication and selection, as well as the structure optimization would be a long term work, which, when fulfilled, may largely improve the dehumidification rate of this humidity pump.

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**Author contributions:**
Biye Cao developed the concept, conducted the experiments, analyzed the data and wrote the paper. Yaodong Tu proposed several helpful suggestions on experiments and revised the manuscript. Ruzhu Wang directed the overall research and revised the manuscript.

**Competing interests:**
The authors have no competing financial interests.
Experiments and Methods

**MIL101(Cr) synthesis.** The synthesis of MIL101(Cr) was following the reported method\(^1\). The chromium (III) nitrate Cr(NO\(_3\))\(_3\)·9H\(_2\)O (purchased from X) and H\(_2\)BDC (1,4-benzenedicarboxylic acid) were involved in the synthesis of MIL-101(Cr). 4.0g of chromium (III) nitrate and 1.66g H\(_2\)BDC were dispersed in 50mL of deionized (DI) water in a 100-mL stainless steel pressure vessel. The mixture was stirred for 10 minutes and consequently treated by ultra-sonic for 15 minutes to avoid aggregations. The pressure vessel was placed in an oven under a programmed heating-cooling process. The temperature rose from RT to 220\(^\circ\)C with a rate of 0.2\(^\circ\)C/min, and was kept at 220\(^\circ\)C for 8 hours. Then cooling process is controlled at 0.2\(^\circ\)C/min drop. Deep green suspension was acquired through this procedure. The SG-MIL101(Cr) composite desiccant was achieved by a pre-mix of MIL101(Cr) suspension and silica-sol in a controlled ratio (mass ratio of 1:10, see SI) and the mixed suspension is stirred overnight to ensure a total dispersion. The suspension was involved in the further steps but MOF powders were also prepared for characterization (see Figure S4).

**Moisture permeable panel fabrication.** The fabrication of moisture permeable panel can be divided into three major steps, including matrix pre-cleaning, desiccant layer formation and photothermal layer coating. The matrix foam was cut into 10cm*10cm pieces of panel with 1.0cm thickness. All the foam panels were thoroughly washed and dried to remove impurities. The loose layer was achieved by partially immerse the panel into silica-sol for 5 seconds. Similarly, the composite layer was obtained by immerse the panel into mixed suspension acquired above for 5 seconds. The condensed layer was obtained by multi-time immersion (3 times in this research). Then all panels were put into an oven under 65\(^\circ\)C for 24 hours. After the completion of desiccant layer, the surface was covered with nano size carbon black powder by suspension spraying method. The ethanol-water liquid mixture (1:4 in volume proportion) was introduced to reduce the hydrophobicity of CB powders. This liquid mixture can contribute a lot to the complete and average dispersion of carbon black powder in the suspension. The suspension was prepared in a concentration of 0.1g/20mL. 10 minutes of shock and 15 minutes of ultra-sonic treatment are carried out to ensure the total and average dispersion. This suspension was put into a spray gun and 20mL of suspension was sprayed onto each panel surface (10cm*10cm). The panel was then placed in an oven under 65\(^\circ\)C for 4 hours. A water cleansing of the surface was introduced to remove the loosely attached carbon black powders.

**Water Vapor Transmission test.** In the test of the Water Vapor Transmission experiment, a test dish, usually a beaker or a glass garden, was filled with controlled amount of distilled water and the specimen was attached to the test dish. The specimen was tightly sealed to the mouth of the test dish by aluminum foil and tapes to prevent any possible leakage. The water surface was controlled 19mm±6mm to the lower surface of the specimen, and the humid air above the liquid surface can be regarded as 100% relative humidity. This apparatus was placed in a temperature and humidity chamber to insure a constant environment outside the dish. An analytical balance was introduced to record the mass loss due to the water vapor difference between the two sides of the specimen. Sketch can be seen in Figure S5.

**Supplementary Text, Figures and Tables**

**The sorption rate test**

The dynamic adsorption (Figure S2a) and desorption (Figure S2b) measurements were carried out in the temperature-humidity constant room. All the samples were fully dried at 70\(^\circ\)C in an oven before adsorption under 25\(^\circ\)C, 70%RH condition and all of them reached equilibrium at 25\(^\circ\)C,
70%RH before desorption at 35°C, 70%RH, with one-sun illumination. The curves only present the performances of the first 3 hours which is critical for the dehumidification process. In adsorption process, the sample with SG-MIL-101(Cr) (red dots) achieves the best water uptake quantity (except the reference sample) while the sample with SG loose layer (blue triangles) only has a modest amount, demonstrating that the introduction of MIL-101(Cr) can largely improve the water uptake rate. The reference sample (black squares) has the same desiccant layer structure as the sample with SG loose layer, but very different water adsorption ability is observed. This is associated with the influence of PF foam which is introduced for thermal insulation, as described previously. The porous structure of PF foam, although accessible for water vapor transmission, clearly alleviates the water vapor transport ability and thus influence the water capture performance. However, identical equilibrium water adsorption quantity (0.181g/g) is acquired for both samples, indicating that the introduction of PF foam only reduces the water adsorption rate due to the tackle of the porous skeletons but scarcely influence the overall water uptake amount.

In desorption process, the sample with SG-MIL-101(Cr) (red dots) losses water very fast while the reference sample (black squares) losses only a little. The surface temperature is considered as the dominating reasons. As illustrated in Figure S2, the IR images were taken to visualize the temperature distribution of the panels under one-sun illumination. The reference sample (a) and the CB coated sample (b) were both illuminated under one-sun condition and a temperature difference of 24°C between the two samples are observed. The average temperature of (a) is around 38.2°C while that of (b) can reach as much as 62°C. The side-view (c) clearly shows the temperature distribution along the normal vector of the panel surface. Steep temperature drop is observed ascribed to the excellent thermal insulation property of PF foam. The SG loose sample (blue triangles) and SG-condensed sample (green triangles) can desorb water much faster than the reference sample but still far from the SG-MIL-101(Cr) sample. This again shows the advantage of MIL-101(Cr) when losing water.

The LDF (linear driving force) model is applied to quantify the sorption rate [12]:

\[
\frac{dx}{dt} = k(x - x_t)
\]

(1)

where \(k\) stands for the rate coefficient (in \(s^{-1}\)), \(x\) for the equilibrium water uptake quantity (in g/g) and \(x_t\) for the dynamic water uptake quantity (in g/g). By combining eq. (1), the following equation is obtained:

\[-\ln \left(1 - \frac{x_t}{x}\right) = k t\]

(2)

The adsorption rate and desorption rate for all the samples are listed in Table S2.

The mass ratio control of the SG-MIL101(Cr)

The original MIL101(Cr) suspension was condensed to 0.1g/mL and was mixed with silica-sol (30% mass ratio) in a volumetric ratio of 3:5. Under such condition, the mass ratio of MIL101(Cr) and SG is 1:10. However, the addition of extra MIL101(Cr) suspension dilutes the silica sol, which may lead to a less mass ratio of the SG. Thus, the mixed suspension should be condensed again to re-gain the original mass-volume ratio of silica-sol. According to the volumetric ratio applied in the previous step, the volume of the condensed mixed suspension should be 62.5% that of the original mixed suspension.

**Figure S1**
The water adsorption isotherm of pure MIL-101(Cr) measured by A. Khutia et al.\textsuperscript{2} Closed and open marks represent the adsorption and desorption processes, respectively.

Fig. S2.
**Figure S2.** Dynamic water adsorption of MIL101(Cr) (a) and nitrogen adsorption test (b). The dynamic water adsorption as well as the nitrogen adsorption test of the MIL101(Cr) were carried out to evaluate the quality of the MOF we prepared. The dynamic adsorption (a) was carried out at 25°C, 70%RH and a final water uptake of 1.08 g/g is obtained. From the nitrogen adsorption (b) result, the BET surface area can be calculated as 2906 m$^2$/g.

**Fig. S3.**

![Graphs](image)

**Figure S3.** The dynamic adsorption (a) and desorption (b) curves. To completely meet the real working conditions, all the adsorption measurements were carried out with the process shown in (c) while (d) stands for the curve SG(reference). All the desorption measurements were taken using the setup (e).

**Fig. S4.**

![Fabrication steps](image)

**Figure S4.** Fabrication steps of moisture permeable panel. The volume ratio of water and ethanol applied for CB suspension is 3:1.
Table S1. Gluing amount of different kinds of moisture permeable panels.

| Panel description | SG-loose | SG-condensed | SG-MIL-101(Cr) |
|-------------------|----------|--------------|----------------|
| Gluing rate (g/cm²) | 0.165    | 0.338        | 0.177*         |

*The gluing amount of SG-MIL-101(Cr) comes from the total weight/total area. The SG-MIL-101(Cr) composite desiccant is pre-mixed with a fixed ratio.

Table S2. Detailed information of IR images.

| Panel number - Time | Average T (°C) | Std. Dev. (°C) | Max/Min T (°C) |
|---------------------|----------------|----------------|----------------|
| a – 0 min           | 25.8           | 0.3            | 26.5/24.8      |
| a – 5min            | 37.7           | 1.5            | 40.1/32.8      |
| a – 30min           | 40.3           | 2.7            | 43.3/33.8      |
| b – 0 min           | 25.3           | 0.1            | 25.7/24.8      |
| b – 5 min           | 56.7           | 3.4            | 62.3/44.8      |
| b – 30 min          | 58.5           | 2.7            | 62.6/49.2      |
| c – 0 min           | 24.7           | 0.2            | 25.5/24.2      |
| c – 5min            | 47.0           | 1.9            | 50.7/40.4      |
| c – 30min           | 55.8           | 3.3            | 60.7/44.5      |
| d – 0 min           | 24.9           | 0.1            | 25.4/24.4      |
| d – 5 min           | 58.4           | 2.8            | 62.6/49.6      |
| d – 30 min          | 60.6           | 2.2            | 64.0/52.6      |

The emissivity is 0.9 and the detect distance is 1 meter.

Table S3. Adsorption and desorption rates for all the samples.

| Sample            | SG-MIL-101(Cr) | SG loose | SG condensed | Reference |
|-------------------|----------------|----------|--------------|-----------|
| Adsorption(s⁻¹)   | 1.02x10⁻⁴      | 8.50x10⁻⁵| 5.95x10⁻⁵    | 2.02x10⁻⁴|
| Desorption(s⁻¹)   | 5.41x10⁻⁴      | 2.42x10⁻⁴| 2.47x10⁻⁴    | 6.45x10⁻⁵|
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