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PERSPECTIVE

Atmospheric Water Harvesting: A Review of Material and Structural Designs

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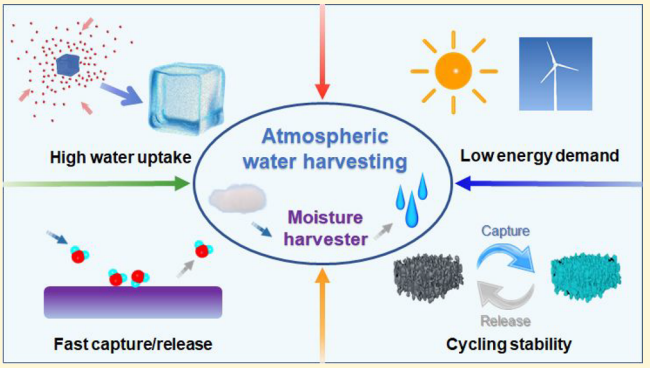
ABSTRACT: **Atmospheric water harvesting (AWH) emerges as a promising means to overcome the water scarcity of arid regions, especially for inland areas lacking liquid water sources. Beyond conventional system engineering that improves the water yield, novel moisture-harvesting materials provide new aspects to fundamentally promote the AWH technology benefiting from their high tunability and processability. Innovative material and structural designs enable the moisture harvesters with desirable features, such as high water uptake, facile water collection and long-term recyclability, boosting the rapid development of next-generation AWH. In this Perspective, we first illustrate the sorption mechanism, including absorption and adsorption for moisture-harvesting materials and summarize fundamental requirements, as well as design principles of moisture harvesters. Recent progress on material and structural designs of moisture harvesters for AWH is critically discussed. We conclude with prospective directions for next-generation moisture harvesters to promote AWH from scientific research to practical application.**



Freshwater scarcity is a global challenge threatening the lives of humankind, especially for people in arid regions.[1,2] However, current freshwater sources, such as rivers, lakes, and groundwater, that are suffering man-made pollution and climatic water loss by environmental damage are becoming insufficient to meet the growing demand.[3] Recently, research efforts have been taken to explore new opportunities to exploit potential freshwater sources. Various water purification technologies, such as filtration,[4] reverse osmosis,[5,6] multistage flash distillation,[7] and solar water purification,[8−13] have been developed to utilize seawater or wastewater. However, because of the dependency on natural water sources, these technologies are mainly feasible in coastal areas and are generally inaccessible for landlocked regions.[14,15] Atmospheric water, which is present regardless of geographical and hydrologic conditions, is emerging as an alternative water resource. The earth's atmosphere holds water in the form of water droplets or vapor, accounting up to ∼10% of freshwater sources and providing ∼50 000 km^3 water.[16] Additionally, the natural hydrologic cycle enables a sustainable water supply.[17] Thus, atmospheric water harvesting (AWH) becomes a promising strategy for decentralized water production, overcoming the challenges of long-distance transport or delivery of potable water in rural areas.

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The AWH discussed in this Perspective is primarily focused on moisture harvesting, different from earlier efforts on fog/dew collection to facilitate the coalescence of small water droplets, generating big droplets that can be further gathered by airflow or gravity.[18,19] The core goal of fog/dew collection technology is to accelerate the growth of water droplets adhering to the surface of collectors and decrease the critical size of water droplets falling from the surface. To this end, surface wettability engineering[20−22] and biomimic micro/nanostructures[23,24] have been investigated. However, the dependency on saturated local humidity (relative humidity, RH = 100%) significantly hinders

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the practical application of fog/dew collection in the parched region.[15,25] In contrast, moisture harvesting (i.e., AWH) is not restricted by geographical and climatic conditions since the moisture is gaseous water (also known as water vapor), which is widespread on the earth.[14] The key target of AWH is to liquefy moisture, generating collectible liquid water.[25,26] The conventional method to harvest moisture is cooling the ambient air below its dew point and collecting the condensate.[27,28] However, the energy consumption is high because a large amount of energy is used to power the cooler and overcome the latent heat (~2450 kJ/kg at 20 °C) during the condensation process, which increases the cost of obtained water, weakening its practical significance.[25,29] Moisture-harvesting materials offer a new aspect to address the above issues based on various tuning knobs for tailoring the interaction between functional materials and water molecules.

Materials-enabled moisture harvesting relies on the water affinity provided by the functional components. Instead of creating high local RH by cooling the surface, moisture-harvesting materials enable spontaneous vapor sorption to trap water molecules, extracting vapor from the air, and hence, concentrating the moisture.[15,25] They are capable of harvesting water in low RH condition as well as saturated RH condition through adsorption or/and absorption. With the release process powered by energy inputs such as heating, the harvested water can be collected efficiently, benefiting from the sufficient accumulation of moisture (Figure 1). A fundamental challenge is the high energy consumption for water release due to the strong affinity between harvesters and water. While useful strategies inherit ideas from conventional desiccants, such as silica gels,[30,31] zeolites,[32,33] and hygroscopic materials,[34,35] new concepts based on unique features of nanostructured materials including MOF-based materials[15,36,37] and hybrid gels[16,35,38−42] have also been proven promising. The ideal moisture harvesters are required to have high water uptake, low energy demand for water release, fast water capture/release, high cycling stability, and low cost, which can be simultaneously achieved by rational material and structural designs, yet to be fully demonstrated. It is essential to fundamentally understand the interaction between materials and water molecules from both experiments and theoretical modelling. Therefore, this Perspective presents the strategies to design moisture-harvesting materials for AWH. Traditional aspects of moisture capture and relevant underlying mechanisms as well as fundamental design principles are discussed first. Innovative material and structural designs, along with representative examples, are then elaborated to introduce current challenges and corresponding strategies. Instead of presenting a comprehensive review of all existing literature, we focus on the representative strategies that are promising in the near future, such as tailoring the water affinity of materials to broaden the working range of RH and enhance the water uptake, architecting micro/nanostructures to facilitate vapor diffusion and moisture capture, newly developed concepts of temperature-responsive water release and explorations on utilizing sustainable power sources with incorporation of functional materials. Finally, the potential challenges relevant to the next-generation moisture harvesters are summarized to propose the opportunities in the future development of this emerging and promising field.

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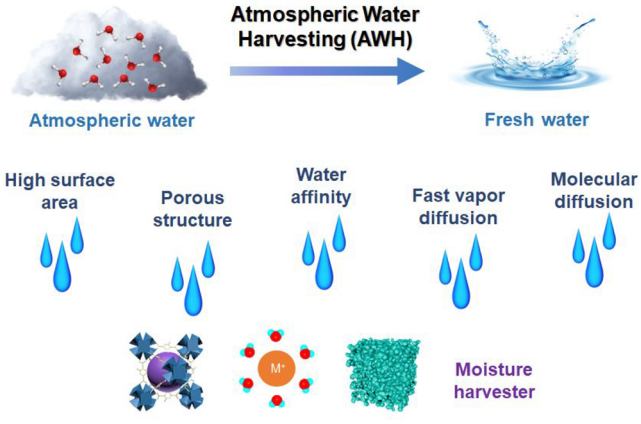

Figure 1. Schematic of atmospheric water harvesting (AWH) based on moisture harvesters. By using moisture harvesters with high surface area, porous structure, water affinity, fast vapor diffusion, and molecular diffusion, the water vapor in atmosphere can be collected as freshwater. The moisture-harvesting materials could be MOF-based materials, hygroscopic materials, and polymeric gels.

UNDERSTANDING MOISTURE SORPTION

AWH based on moisture harvesters captures vapor from the air via absorption or adsorption, which refers to the attachment of water molecules to materials through physical or chemical processes (Figure 2a).[25,43] Absorption can be considered as a bulk phenomenon where gas/liquid molecules diffuse into liquid/solid materials, changing the structure and volume of absorbent materials. Water molecules can be absorbed by chemical reaction and/or physical interaction with absorbent materials.[44] The chemical absorption depends on the stoichiometry of the reaction and the concentration of the reactants, while the physical absorption is usually driven by osmotic effect. Typical moisture harvesters based on absorption are hygroscopic materials, which capture water molecules through the hydration process involving chemical absorption and physical absorption.[35,39] For example, deliquescent salts can absorb moisture when the vapor pressure of contained water is lower than the partial pressure of vapor in air,[45,46] exhibiting high water uptake. However, particle agglomeration during hydration/dehydration process of solid salts might result in performance decay due to reduced permeability of water vapor.[25] Moreover, the desorption process for hygroscopic materials is regarded as the bottleneck because of the high vaporization enthalpy.[45,46]

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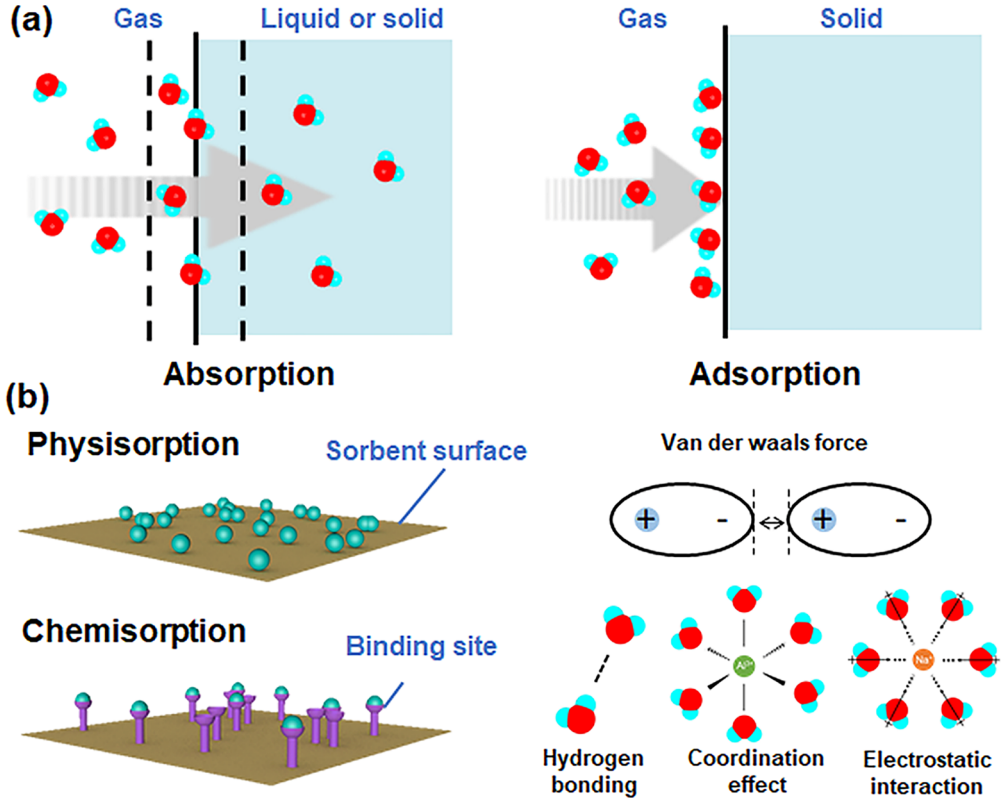

Figure 2. Moisture sorption mechanisms. (a) Schematic of absorption(left) and adsorption (right) processes. (b) Schematic of physisorption (top left, top right) and chemisorption (bottom left, bottom right).

Adsorption is a surface phenomenon in which molecules of gas or liquid adhere to a surface through chemical (chemisorption) or physical (physisorption) interactions-(Figure 2b).[25] The thermodynamics of adsorption is relevant to the intrinsic material properties. For chemical adsorption, the sorbent surface needs binding sites to adsorb molecules through strong chemical bonding, such as hydrogen bonding, coordination effect and electrostatic interactions. The energy barrier involved is relatively high (80−400 kJ/mol), which is generally irreversible without energy supply.[47,48] Langmuir isotherm[49−51] can be used to describe the chemisorption upon following assumptions: (1) all adsorption sites are identical, (2) each site of the absorbent can only accommodate one and only one molecule, and (3) all sites are energetically and sterically independent of the adsorbed quantity by eq 1

$$\theta = \frac{\alpha \cdot p}{1 + \alpha \cdot p} \tag{1}$$

where θ is the equilibrium fraction of the adsorbate monolayer coverage, which can reflect the sorption capacity in a certain content, α is the Langmuir adsorption constant depending on the intrinsic affinity of the adsorbent toward the adsorbate and the temperature, and p is the partial pressure of adsorbate.[52] It is obvious that enhancing the interaction between materials and water molecules (larger α) and increasing local RH near the adsorption sites (larger p) will promote the moisture capture capacity. The amount of molecules adsorbed on surfaces also depends on the surface area of sorbents. Physisorption presents weak van der Waals force between the sorbent surface and adsorbed molecules. This process is readily reversible and requires energy of ∼20 kJ/mol or less. Brunauer, Emmett, and Teller (BET) isotherm[52,53] is a well-accepted model to explain the physical adsorption, which is based on following assumptions: (1) the enthalpy of adsorption for the first layer (E_1) is constant and greater than the following layers and (2) molecules can adsorb on each other. In this case, the enthalpy of adsorption layers over the first layer is the same as the enthalpy of liquefaction (E_L). The dependency could be described by eq 2

$$\frac{\frac{p}{p_0}}{N(1 - \frac{p}{p_0})} = \frac{1}{N_0 C} + \frac{C - 1}{N_0 C}\frac{p}{p_0} \tag{2}$$

where p and p_0 are the equilibrium and the saturation vapor pressure of the adsorbate at the temperature of adsorption, respectively, N refers to equilibrium gas adsorption amount at the relative pressure p/p_0, N_0 is the monolayer gas adsorption quantity, that is, the number of molecules needed to uniformly cover the substrate with one complete monolayer, and C is the BET constant related to the energetics of the system

$$C = \exp\left(\frac{E_1 - E_L}{RT}\right) \tag{3}$$

where R is the gas constant and T is the temperature. Therefore, improving the surface area (greater N_0) can help to achieve a higher sorption capacity (reflected by larger N).

Regarding the adsorption kinetics, the exposure of the absorbent to the air becomes dominative since the diffusion of moisture significantly affects the adsorption process. Linear driving force (LDF) model[54,55] assumes that the temperature of adsorbent particles is uniform (does not vary with radius) at all times and the vapor partial pressure is constant, is used to describe mass-transfer by eq 4

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$$\mu = \frac{d_x}{dt} = k_1(x^* - x) \tag{4}$$

where μ is the sorption rate (s^{-1}), x^* and x are the equilibrium and the dynamic water uptake of the adsorbent, respectively, and k_1 is the LDF adsorption rate coefficient (s^{-1}) and is positively related to the diffusion coefficient (D_e) and negatively related to the adsorbent particle size (r_0):[25]

$$k_1 = \frac{15D_e}{r_0^2} \tag{5}$$

It is worthy noting that the sorption behavior of current moisture harvesters is usually exhibited as the combination of physisorption and chemisorption, and may involve absorption as well.[34,35] The corresponding underlying moisture capture mechanism is rather complex compared to the theoretical models. Nevertheless, based on the understanding of the fundamental sorption mechanism, the material and structural designs could be rationally optimized to enhance the sorption properties of moisture harvesters.

Moisture capture capacity, the energy demand of water release, sorption and desorption kinetics, and cycling durability are essential features of moisture harvester enabled AWH technologies.

MATERIAL DESIGN PRINCIPLES AND CHARACTERIZATION

Moisture capture capacity, the energy demand of water release, sorption and desorption kinetics, and cycling durability are essential features of moisture harvester enabled AWH technologies. Superior moisture sorption based on materials with enhanced water affinity, large surface area and high porosity can increase the water uptake to harvest enough moisture for vapor liquefaction, delivering collectible water. Low water-release energy demand can be achieved by tailoring the sorption behavior of materials and incorporating functional materials, such as thermal responsive materials to introduce phase separation, which eliminates energy-intensive phase transition process during water collection. In addition, fast water sorption and desorption are essential for high water production within a short period of time. Moreover, since the AWH is a time-intensive process, the moisture harvesters should be stable during long-term cycling process without potential performance decay (Figure 3). Through proper material selection and rational modification, an ideal moisture harvester with high water uptake, low generation energy demand, fast sorption/desorption, and cycling stability can be obtained for efficient AWH.

The sorption capacity of moisture harvesters is the most important factor for efficient water harvesting from the air, which is usually evaluated by dynamic vapor sorption. Water sorption isotherms can be obtained to present the equilibrium mass of water which can be captured by materials as a function of RH at a given temperature. At the low RH levels, water molecules are absorbed on the surface of materials and then liquefied as liquid water. When the humidity is saturated, the

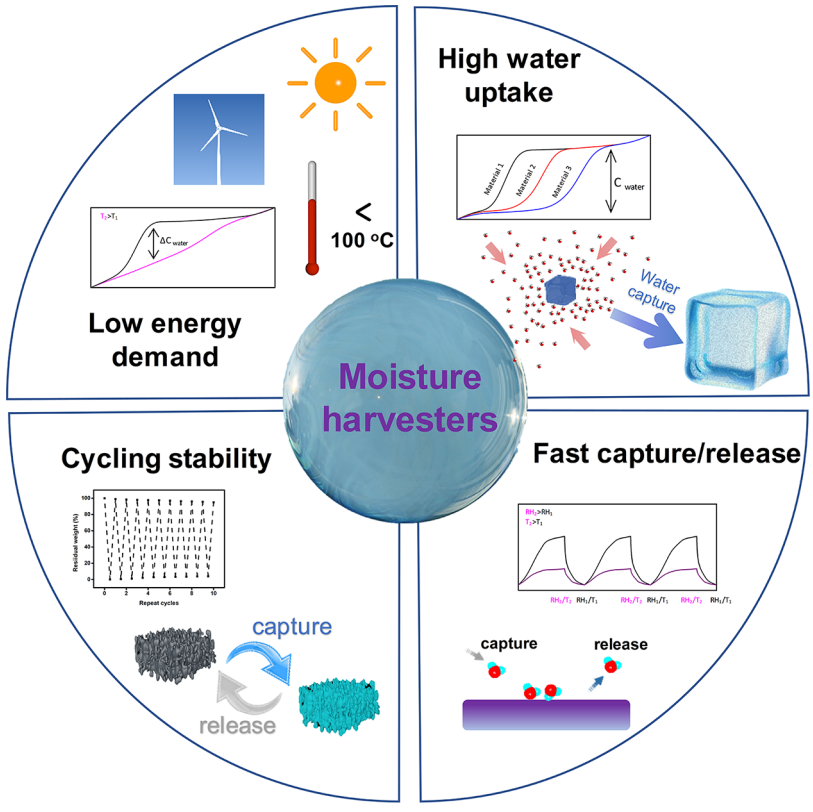

Figure 3. Essential properties of moisture harvesters for AWH. The ideal moisture harvesters should have high sorption capacity, low regeneration energy demand, fast sorption/desorption, and long-term cycling stability.

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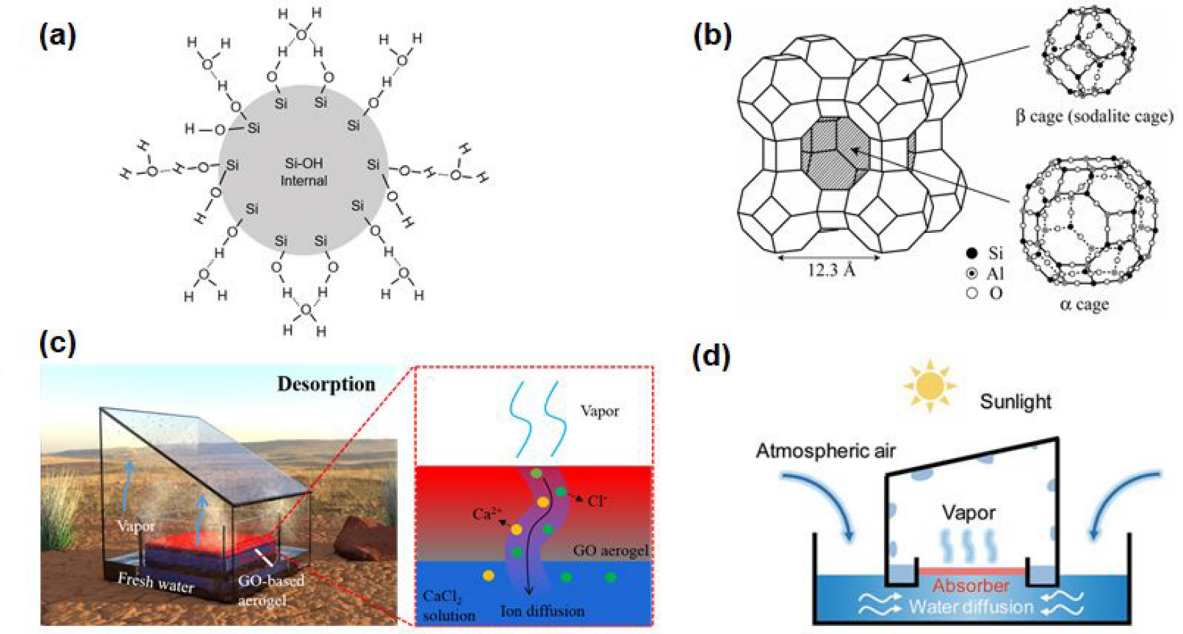

Figure 4. (a) Schematic of silica gels adsorbing water molecules. Reprinted with permission from ref 56. Copyright 2000 Elsevier Science B.V. (b) Porous structure of zeolites. Reprinted with permission from ref 58. Copyright 2008 IOS Press. (c) Deliquescent liquid sorbents for AWH assisted by an interfacial solar heating strategy. Reprinted with permission from ref 45. Copyright 2019 Wiley-VCH Verlag GmbH & Co. (d) Simultaneous sorption-desorption of liquid sorbents. Reprinted with permission from ref 46. Copyright 2019 Wiley-VCH Verlag GmbH & Co.

materials provide active sites for nucleation and growth of liquid water. The water uptake at saturated RH is the maximum capacity of materials. The shape of isotherms is important to be capable of optimizing water harvesting capability. The isotherm with stepwise water uptake (type IV and V) in the RH range between 10% and 30% is desirable for facilitated water adsorption at low RH condition in arid regions, which means that a large amount of vapor from the air can be captured as the ambient RH is higher than the position of sorption step.[15,25] However, the isotherm of traditional sorption materials, which indicates their sorption behaviors cannot satisfy this criteria, making them inappropriate for efficient AWH. For example, zeolites present fast and saturated water sorption at extremely low RH (Type I), due to their strong binding with water molecules and abundant sorption sites, however, high regeneration temperature is required to release and condense water. Silica gels can only adsorb limited amount of vapor in low RH conditions (Type II), which is not suitable for arid regions. In addition, obvious difference of sorption capacity between adsorption and desorption temperature is required for large amount of collected water, which can be evaluated by static vapor sorption techniques measuring the water uptake over time at a given RH and temperature. The water affinity and micro/nanostructures of moisture-harvesting materials should be tailored for desirable sorption behaviors and high water capacity based on the isotherms. For instance, the hydrophilicity, porosity and geometry of MOF-based materials can be modified by varying the metal ions, ligands, etc.[15] Composite gels incorporated with hygroscopic salts or polymers can be tailored by applying different polymer matrices and hygroscopic materials, changing the polymer concentration, crosslinking density, functional additives, etc.

As for traditional sorption materials for AWH, the water release (i.e. regeneration) step usually involves heating process with extensive energy consumption because of their strong interaction with water molecules, which is not suitable for practical application. By choosing materials with desired sorption behaviors, regeneration of moisture harvesters by low grade energy input can be achieved. The solar irradiation can be utilized to desorb the water molecules when the harvesters have photothermal conversion ability[16,35,39,45] or incorporating solar absorbers. In addition, functional materials, such as temperature-responsive materials, can be introduced to release water for efficient regeneration by liquid−liquid phase separation under solar irradiation.[16] Another important factor is the fast sorption and desorption of moisture harvesters, which can be evaluated by the sorption/desorption kinetics measured within different RH and temperature intervals. The high rates enable multiple water harvesting cycles for high water production in a short period of time. Micro/nanostructures with high pore density can facilitate vapor diffusion and water transport for fast sorption and desorption. Moreover, the moisture harvesters should be stable without performance decay during cycling process of sorption and regeneration. Various strategies are applied for different sorption materials. MOF-based materials are modified with hydrolytic stability through changing the strength of metal-linker bond and the energetic positioning of the frontier orbitals on the metal ions with respect to those of water. Hygroscopic salts are incorporated in supporting matrices, such as gels and MOFs, to avoid particle agglomeration for cycling stability. By designing moisture harvesters with above features, efficient AWH for practical applications can be realized.

MATERIAL AND STRUCTURAL DESIGN OF MOISTURE HARVESTERS FOR AWH

Traditional Moisture Harvesters. For AWH technologies based on moisture harvesters, traditional desiccants, such as silica gels, zeolite, hygroscopic salts, and deliquescent liquids, are initially utilized to harvest water because of their high affinity with water. Silica gel is one of the most commonly used moisture-harvesting materials, which has polar hydroxyl groups

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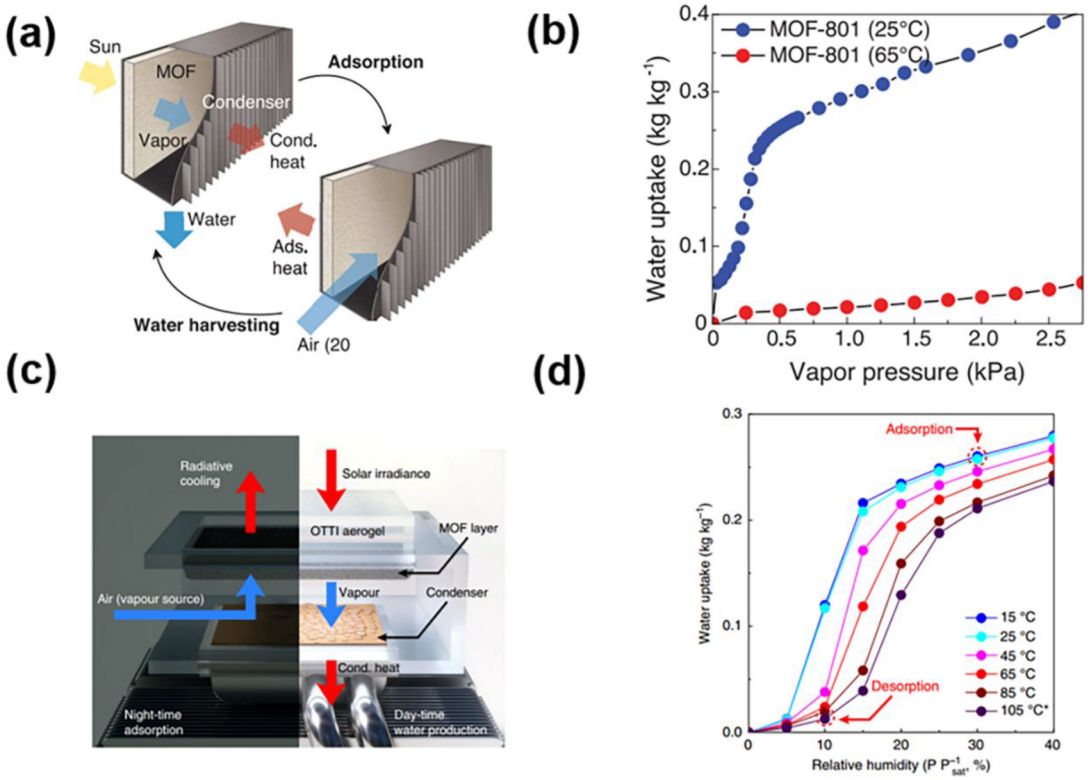

Figure 5. (a) Schematic of AWH based on MOF-801. (b) Water adsorption isotherms of MOF-801 at different temperatures. Reprinted with permission from ref 36. Copyright 2017 American Association for the Advancement of Science. (c) Schematic of the water harvesting device containing a radiative cooling part. (d) Water adsorption isotherms of MOF-801 as a function of RH ($P P_{sat}^{-1}$, vapour pressure over saturation pressure) at temperatures of 15, 25, 45, 65, and 85 °C. Reprinted with permission from ref 37. Copyright 2018 Nature Publishing Group.

as the chemical adsorption centers to form hydrogen bonding with water molecules (Figure 4a).[56] With the increasing number of hydroxyl groups on the surface, the adsorption ability of silica gels could be enhanced due to increased density of sorption sites. This could be reflected from the eq 1, high density of sorption sites increases the overall affinity between silica gels and water molecules, leading to a larger Langmuir adsorption constant (α) and high maximum capacity (θ). The pore diameters of common silica gels are within several nanometers and the specific surface area is about 100−1000 m^2/g.[57] This porous structure and high surface area of silica gels are beneficial for water harvesting. Zeolite is another widely used solid moisture-harvesting material, which are three-dimensional networks composed of silica and alumina that contain alkali and alkaline-earth metals (Figure. 4b).[58] The aluminum metal is the sorption site which has coordination effect with water molecules, whose amount influences the water harvesting ability. The porous structure of zeolite also determines the water harvesting capacity, larger pore volume usually leads to high sorption capacity.[59] However, the water capacities of silica gels and zeolites are relatively low, which are around 0.3−0.5 kg_{water} $kg_{sorbent}^{-1}$.[60] Besides, the high water affinity makes the release of harvested water difficult, requiring high energy consumption. The relative low water uptake and high energy demand for desorption render them unsuitable for efficient AWH.

Unlike silica gels and zeolite, hygroscopic materials that can harvest water molecules via absorption and/or adsorption exhibit high water uptake and are capable of taking up water at low RH.[38,61] Hygroscopic materials include hygroscopic salts and deliquescent liquid sorbents. Hygroscopic salts, such as LiCl, $MgCl_2$, and $CaCl_2$, can harvest moisture by hydration reaction but suffer from problems of particle agglomeration and passivation layer formation on particle surface during hydration, which will reduce the permeability of water vapor and decrease the sorption capability. Deliquescent liquid harvest water until the vapor pressure of the solution is equal to the partial pressure of vapor in air.[25] The fundamental challenge for hygroscopic materials is the high energy consumption for desorption, especially for deliquescent liquid whose whole bulk liquid is heated. Recently, photothermal materials are combined with deliquescent liquid to efficiently utilize solar energy for heating during the desorption process by interfacial evaporation. The moisture harvester is composed of an interfacial solar heating layer (GO-based aerogel) on the surface of a liquid sorbent (50 wt % $CaCl_2$ solution), realizing a AWH performance of 2.89 kg m^{-2} day^{-1} (Figure 4c).[45] Different from bulk heating, the harvested solar energy can be concentrated on the evaporation surface, greatly reducing the energy loss to bulk water and improving energy utilization efficiency. In this system, the $CaCl_2$ solution can capture moisture from air during night by adsorption, and the salt-resistant GO-based aerogels enable the water releasing by efficiently utilizing solar energy through interfacial heating during the daytime. Then, the moisture harvester is further designed to realize simultaneous harvesting−releasing process for continuous water production and realize a water production rate of 0.5 L m^{-2} h^{-1}.[46] The system is composed of two interconnected parts, one part is filled with the liquid sorbent for water capture and another contains a photothermal layer floating on the liquid for water release (Figure 4d). Moisture in the environment can be captured by the liquid sorbent and be released continuously as vapor by interfacial solar heating, which then is condensed to liquid water

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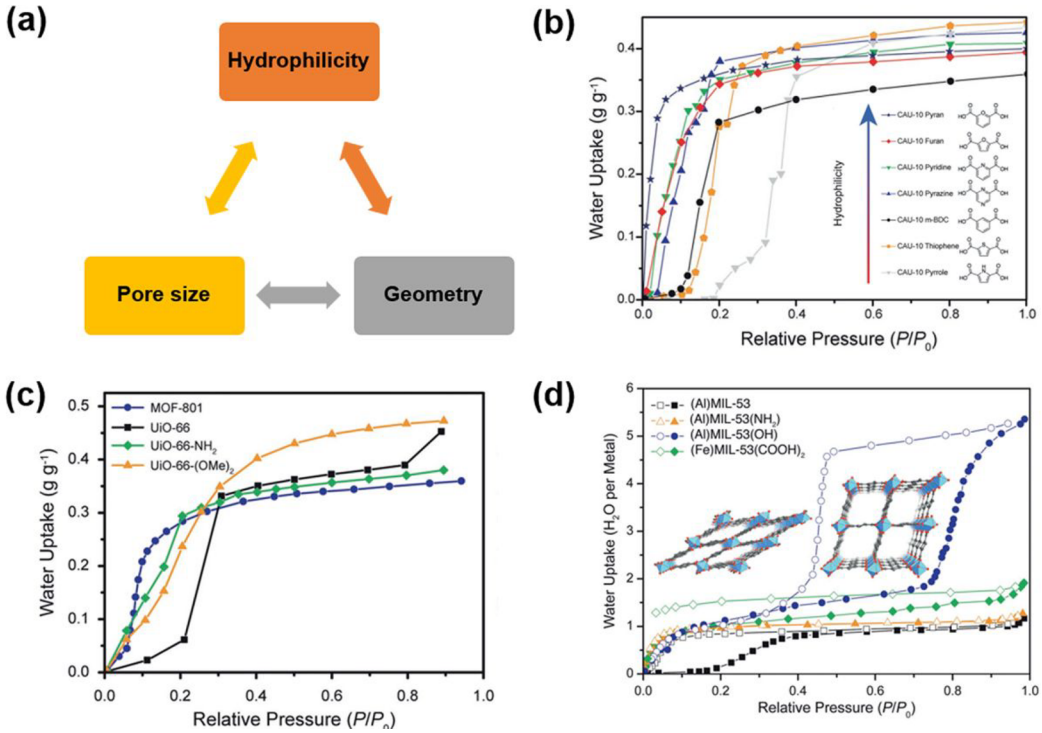

Figure 6. (a) Tuning factors of MOF-based moisture harvesters. Water sorption isotherms of MOF-based moisture harvesters with different (b) hydrophilicity, (c) pore size, and (d) geometry. Reprinted with permission from ref 15. Copyright 2018 Wiley-VCH Verlag GmbH & Co.

to be collected. However, the dependence of water uptake capability on environmental RH hinders the practical AWH of liquid harvesters in arid regions. Besides, the difficulties in handling as well as engineering of deliquescent liquids also cause issues in practical AWH.

Although these single-component water harvesting materials work well as desiccant for dehumidification, they can barely meet the requirements for efficient AWH due to the insufficient water release. The fundamental challenge is the intrinsic high energy demand during the desorption or dehydration processes caused by their high affinity with water molecules, which is difficult to be solved. Thus, new materials with highly tailorable properties have been proposed as alternatives to meet the demand for efficient AWH.

MOF-Based Moisture Harvesters. MOFs are a kind of crystalline porous materials constructed by metal-containing inorganic building centers and polyfunctional organic ligands through coordination bonds into three dimensional (3D) interconnected networks. The highly porous structure of MOFs can provide numerous potential sorption sites for water molecules. Water sorption in MOFs can occur following three distinct mechanisms: (i) chemisorption on open metal sites, (ii) physisorption in the form of layers or clusters, and (iii) capillary condensation when the pore size is large than the critical diameter of water.[15] The desorption process requires heat input to reach the regeneration temperature, which varies from several tens to hundreds of degrees Celsius depending on the adsorption strength of the water molecules.[62] Although the water sorption/desorption mechanism of MOFs has been investigated, they draw much attention until very recently for AWH because their stability in water is a challenge and the sorption/desorption behaviors need be carefully tailored for efficient AWH. By tailoring the structures and compositions of MOFs, their properties such as hydrophilicity, and pore size/volume can be tuned for desired sorption and desorption behaviors to realize superior water harvesting performance.

One of the first MOF-based AWH devices was demonstrated based on Zr-based MOF (MOF-801) that can achieve water harvesting at a low RH environment (Figure 5a).[36] MOF-801 is chosen as the harvesting material because it can take up water within a narrow RH range and enable water release of large amount with small temperature increase, which also exhibits good stability and recycling (Figure 5b). MOF-801 shows good performance driven by aggregation of water molecules into clusters within the pores. Eventually, a water production rate of 2.8 $g_{water}\, g_{MOF}^{-1}\, day^{-1}$ at relative humidity levels as low as 20% is achieved with solar energy as the only energy input for desorption. Furthermore, a passive radiative cooling strategy is introduced into the MOF-based AWH system that can work in the arid climate (Figure 5c).[37] The passive radiative cooling can be realized by dissipating thermal radiation to the clear cold sky to increase the effective RH for adsorption. By utilizing the copper foam with high emissivity for passive radiative cooling at the top of the device, a ~3 K temperature drop can be achieved, which corresponds to an increase in 5−7% RH experienced by the moisture harvester during the AWH process. This device can operate in an exceptionally arid climate (10−40% RH) and sub-zero dew points with a thermal efficiency (solar input to water conversion) of ~14% (Figure 5d).

Since the stability, hydrophilicity, and pore diameter of MOFs determine their water harvesting performance, understanding how to rationally design MOF-based moisture harvesters for desired properties is essential to achieving efficient AWH. The sorption/desorption behaviors of MOFs can be adjusted by controlling their hydrophilicity, pore size, and geometry (Figure 6a). The hydrophilicity of MOFs can be tuned by modifying the metal nodes and organic ligands with different functional groups. As the hydrophilicity of MOF increased (Figure 6b), the

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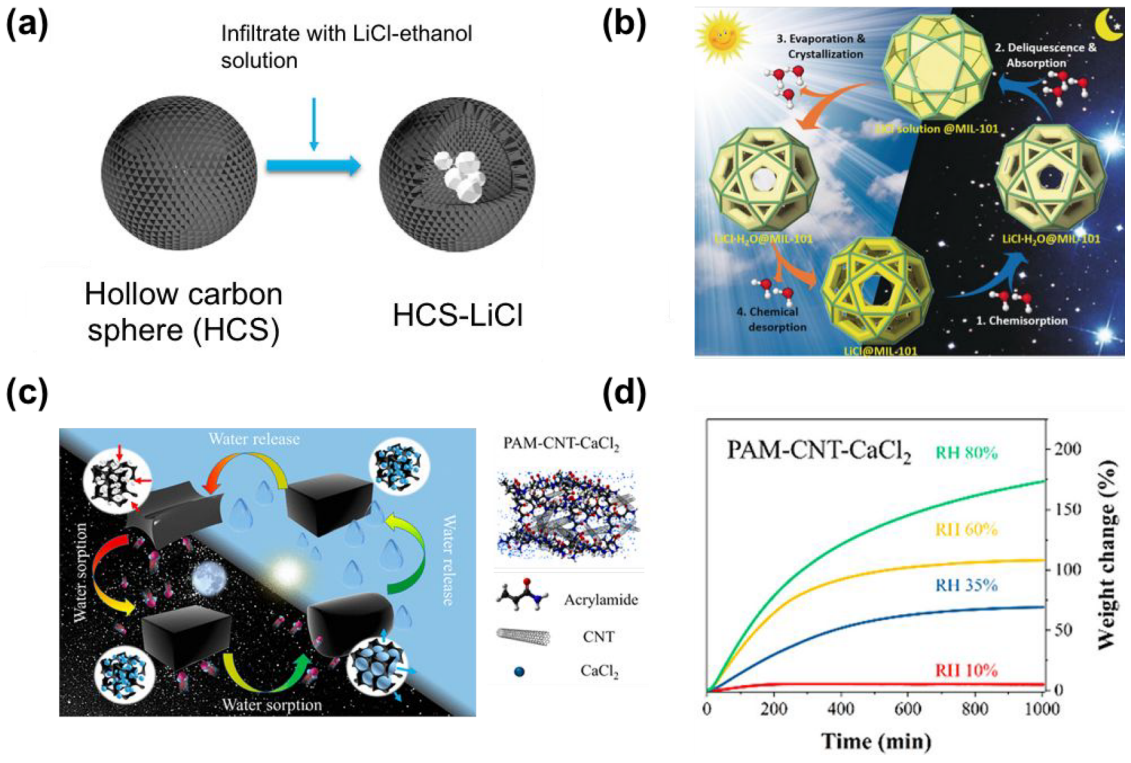

Figure 7. (a) Impregnating of LiCl into a porous carbon matrix. Reprinted with permission from ref 67. Copyright 2020 Elsevier. (b) MOF as the supporting matrix for LiCl for AWH. Reprinted with permission from ref 68. Copyright 2020 Wiley-VCH Verlag GmbH & Co. (c) AWH based on PAM-CNT-$CaCl_2$ moisture harvester. (d) Water vapor harvesting curves of PAM-CNT-$CaCl_2$ moisture harvester under different RH. Reprinted with permission from ref 38. Copyright 2018 American Chemical Society.

adsorption isotherms shift to a lower relative pressure value, indicating that the adsorption process can occurs at a lower RH.[15,63] Therefore, higher hydrophilicity is beneficial for water capture due to the enhanced interactions between MOF and water molecules. Pore size in MOFs also plays a great role in affecting the water adsorption behaviors. Increasing the length of organic linkers can enlarge the pore size, offering a larger maximum sorption capacity (Figure 6c).[15,64] However, the increase of the pore size might change the water adsorption mechanism from pore filling to irreversible capillary condensation, which has a hysteresis loop and the captured water is extremely hard to be released. Thus, the pore size should be moderate for both high moisture capture capacity and relatively easy water release. It is worthy noting that although the modification of organic linkers can tune the hydrophilicity of the MOF for efficient water harvesting under a specific condition, it may cause a substantial decrease of porosity and thus reduce the adsorption capacity. The trade-off between the hydrophilicity and porosity should be considered when modifying the MOFs with functional groups.

Geometry is another parameter that affects the water sorption behavior of MOFs. Water-sorption isotherms of isoreticular (M)MIL-53(R) (M = Al, Fe) with different −R groups changing from $-(NH_2)$ to $-(OH)$ and to $-(COOH)_2$ are shown in Figure 6d.[15] The different −R groups have effects on their geometries because of their different steric configurations. Only the (Al)MIL-53(NH_2) (orange triangles) shows a reversible water adsorption/desorption behavior while the other isotherms show the obvious difference between the adsorption/desorption processes due to the reversible structural phase transition during these processes. Take (Al)MIL-53(OH) as an example, its isotherm shows a strong breathing effect at P/P_0 = 0.8 and a strong hysteresis between the adsorption and desorption branch. This means that the desorption of water can only occur at lower RH due to the enlarged pore size during adsorption.

Although the MOF-based moisture harvesters can be used for AWH with rationally tailored water sorption behaviors, it has been proven difficult to synthesize most of the suitable MOFs on a commercial scale that allows for large-scale, cost-efficient water production. The exploration of more stable MOFs which possess controlled porosity and excellent water capture/release properties is the cornerstone for future industrial application. There are still several key challenges that need to be overcome. First, developing MOFs with improved water sorption capacities under different temperature/RH working conditions is necessary to optimize their inherent sorption performance for practical AWH. Second, a more detailed and fundamental understanding of the sorption/desoprtion kinetics is still lacking for further development of MOF-based moisture harvesters. Third, beyond long term stability and cycling issues, shaping/processing of MOFs is also a key aspect in the practical application in the future.[47] Therefore, new MOFs with intrinsic better water sorption/desorption properties is highly desirable for superior AWH. In addition, most of the existing MOF-based moisture harvesters can only realize one sorption/desorption cycle per day, greatly limiting their potential water production amount. Achieving multiple cycles is also a key point for better AWH performance and practical applications.

Hygroscopic Salts and Composites. Hygroscopic materials feature their interaction with water molecules in surrounding environment throughout the material, in addition to the surfaces, which enables high water uptake as many as 5−6

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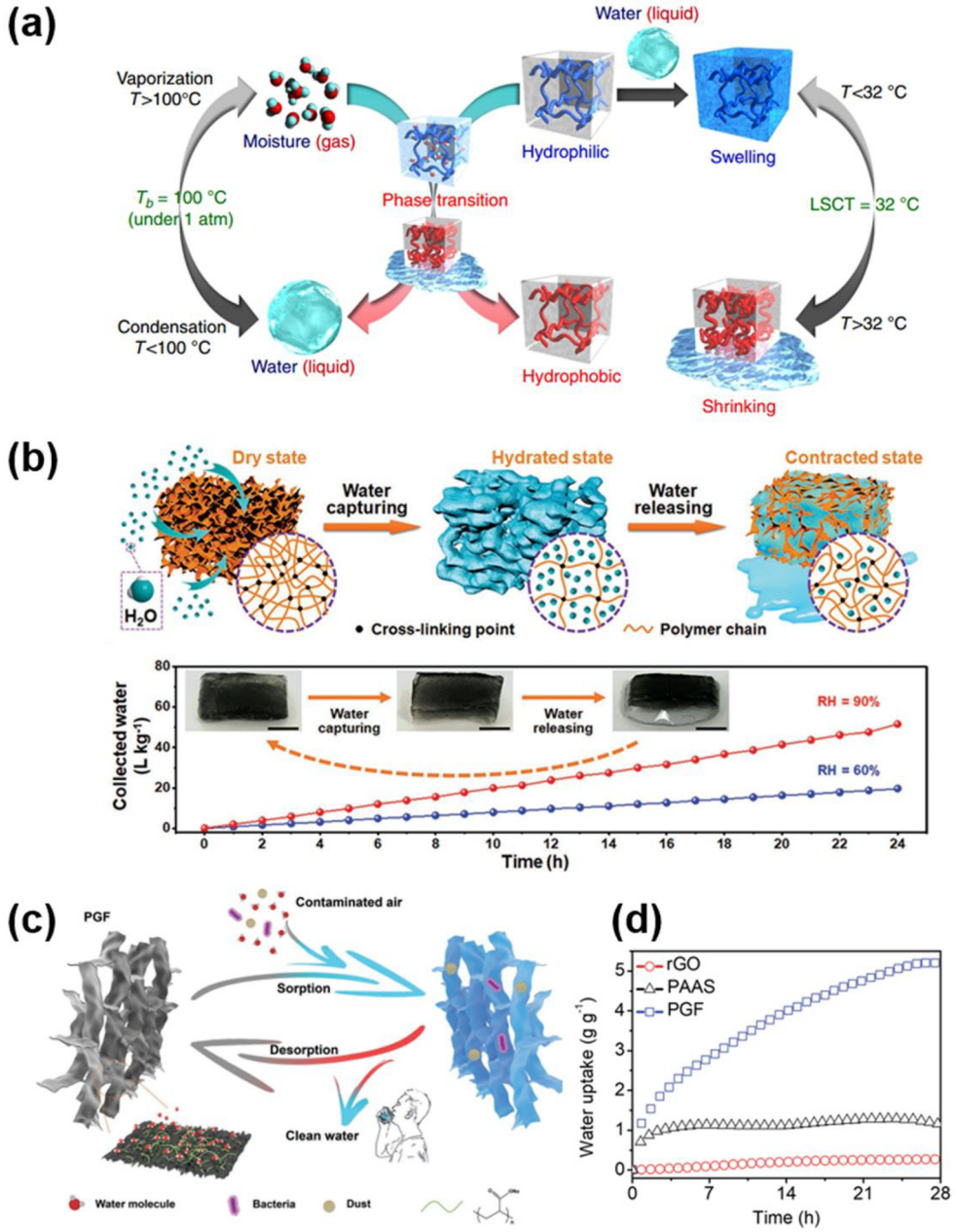

Figure 8. (a) AWH based on a thermoresponsive interpenetrating network gel with liquid water release. Reprinted with permission from ref 40. Copyright 2018 Nature Publishing Group. (b) AWH based on the SMAG and its water uptake in different RH. Reprinted with permission from ref 16. Copyright 2019 Wiley-VCH. (c) AWH based on a rGO-PAAS gel. (d) Water uptake of rGO, PAAS, and PGF (25 °C, RH = 100%). Reprinted with permission from ref 69. Copyright 2020 Wiley-VCH.

times of their own weight. However, the structural deterioration of these materials over wetting-drying cycles, such as particle agglomeration, drastically degrades the moisture capture rate because of insufficient exposure to the moist air. The water molecules will accumulate on the surface of materials and diffuse into the closely packed structures (e.g., crystalline structure), leading to a slow water condensation near the sorption interface. Given the augmented water affinity of this type of materials, it is not surprising to find their high energy demand of water release. Such a high energy consumption limits the practical application of hygroscopic materials in AWH. In this context, porous materials have been utilized as the supporting matrix for hygroscopic salts or polymers to overcome these challenges. Fast vapor diffusion and water release are enabled by the designed micro/nanostructures. The cycling stability of moisture harvesters is also enhanced because of the embeddedness of hygroscopic components fixing in the matrix. By incorporating photothermal materials such as solar absorbers, new energy sources can be employed for efficient AWH.

Hygroscopic salts have been demonstrated to incorporate with porous supporting matrices, including silica gels,[60,65] zeolites,[66] porous carbon,[67] MOFs,[68] and polymer hydrogels,[35,39] as composite moisture-harvesting materials, taking advantages of the stability of the porous matrix and high water capture capacity of hygroscopic salts. For example, by simply impregnating LiCl into the void core of a nanocarbon hollow capsule, a moisture harvester that can capture and release water vapor from ambient air with significantly enhanced kinetics is

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obtained (Figure 7a) because of the shortened vapor diffusion length inside the sorbent.[67] Attributing to the fast sorption/desorption process, a batch-mode AWH device based on this moisture harvester could conduct 3 harvesting/releasing cycles within 10 h and have water harvesting capacity of 1.6 kg_{water} $kg_{sorbent}^{-1}$. MOF can also be a good host for hygroscopic salts. A high-performance composite moisture harvester is prepared by encapsulating a hygroscopic salt into a MOF matrix (LiCl@MIL-101(Cr)) (Figure 7b).[68] Benefiting from the uniform porous structure and large pore volume of MOF, the moisture harvester exhibit faster water harvesting kinetic and cycling stability than bulk LiCl. A highly efficient AWH prototype based on LiCl@MIL-101(Cr) is demonstrated, enabling water harvesting of 4.5 kg_{water} $kg_{sorbent}^{-1}$ under outdoor ambient conditions powered by natural sunlight as the only energy input. The porous supporting matrix greatly enhances vapor diffusion and water release, improving the AWH performance.

In addition to conventional porous materials, polymeric gels have been reported as a promising host matrix for hygroscopic salts. A hybrid photothermal moisture harvester (PAM−CNT−$CaCl_2$) composed of a deliquescent salt ($CaCl_2$), a hydrogel host (polyacrylamide, PAM) and photothermal carbon nanotubes (CNT) is developed (Figure 7c).[38] With the RH of 10%, 35%, 60%, and 80%, the water sorption amounts of PAM−CNT−$CaCl_2$ are 5%, 69%, 110%, and 173%, respectively (Figure 7d). The $CaCl_2$ is introduced in the hydrogel network by aqueous solution based physical impregnation and is mostly responsible for the water capture either by hydration reaction at low RH (<26%) or deliquescence at high RH (>26%). Through the introduction of $CaCl_2$ with high water affinity, the Langmuir adsorption constant of the system can be improved and enable a higher capacity. The incorporation of photothermal materials enables the utilization of renewable solar energy. The cross-linked hydrogel network keeps the deliquescent $CaCl_2$ solution in a solid form, and the flexible expansion behavior of the hydrogel makes the pore volume not a limiting factor and, thus, enhances the water harvesting capacity. As a result, 35 g of dry hydrogel could deliver 20 g of water in 2 h and a half under natural sunlight after capture water at 60% RH. The water capacity can be further improved by incorporating binary salts in the hydrogel network.[39] A composite hydrogel composed of alginate chains modified with binary salts and functionalized multi-walled carbon nanotube (FCNT) as an efficient solar absorber is demonstrated as the moisture harvester (Bina/FNCT). The Bina/FNCT is found to have both higher water adsorption capacity (5.6 g_{water} $g_{sorbent}^{-1}$) and better stability than the sorbents obtained by a single salt because the combination of the salts increases water affinity of the material and the porous structure facilitates vapor diffusion into the beads.

While much of the credit is given to the unique hygroscopic composites associated with large active area for moisture harvesting, it is unclear how much the porous structure has contributed to the vapor capture performance. The emerging studies indeed demonstrate the feasibility of porous structure architecting in hygroscopic materials for AWH. Nevertheless, the role of the porous structure should be more manifested in sorption processes involving more complex composition, structures, and functionalities, such as heat management for high energy efficiency. In addition, the fundamental process of water release still relies on the dehydration of hygroscopic components instead of reducing the intrinsic energy demand of water release, and ingenious designs for energy recycling or introduction of new energy input should be introduced.

Novel Molecular Water Reservoirs. Though the moisture capture capacity and cycling stability can be improved by directly impregnating hygroscopic salts into a porous supporting matrix and they could be enhanced by structural designs and system engineering, more versatile methods have been developed via molecular engineering involving hydrophilicity controllable polymers or molecular heaters. By combining hygroscopic materials and hydrophilicity controllable polymers at a molecular level, the water release process can be achieved by a phase separation process, where the polymer in hydrophilic state serving a molecular reservoir is controllably switched to a hydrophobic state, releasing the containing water without any energy-intensive processes such as desorption or dehydration. Such a water regulation in the molecular level, which is a key innovation synergistically inheriting the intrinsic properties of building blocks, opens new opportunities for AWH.[16,40] Taking the thermoresponsive polymer as an example of novel molecular water reservoirs, an interpenetrating polymer network (IPN) gel that can capture moisture from the air and directly extract liquid water was reported by combining a thermoresponsive component (poly(*N*-isopropylacrylamide), PNIPAM) with a hydrophilic sodium alginate network (Figure 8a).[40] Because of the hydrophilic property of the IPN gel at temperature below its low critical solution temperature (LCST, 32 °C), the dried IPN gel can harvest considerable moisture from air. Upon increasing temperature, the IPN gel changes from hydrophilic to hydrophobic due to the thermo-responsive property of PNIPAM, enabling water molecules to be converted from a gaseous state to a liquid state by a small temperature change above the LCST and releasing the absorbed moisture as liquid water. The water-releasing behavior of this thermoresponsive moisture harvester is significantly different from that of common harvesters, which rely on the desorption of water vapor upon high temperature. However, the overall efficiency and moisture absorption capacity of this moisture harvester are relatively low.

Recently, a super moisture-absorbent gel (SMAG) composed of polypyrrole chloride (PPy-Cl) penetrating in PNIPAM network with the hydrophilicity-switchable ability (Figure 8b) is developed to enable synergistic effect of hygroscopicity and thermoresponsive water releasing to enhance water harvesting capacity.[16] This moisture harvester can simultaneously realize efficient moisture capture, in situ water liquefaction, high water storage capacity, and fast liquid water release under different weather conditions, achieving high-efficiency water production in a broad RH range. The adsorbed water molecules are first liquefied on the surface of the SMAG and then diffuse into the PNIPAM matrix to be stored and cause swelling. The molecular-level interaction between PPy-Cl and hydrophilicity-switchable PNIPAM allows internal water rearrangement when several layers of water molecules are captured from air through physisorption, reactivating the sorption points to harvest more water molecules. The liquid water can be rapidly released by liquid−liquid phase separation enabled by the thermal-responsive hydrophilicity switching of PNIPAM network when the temperature is above its LCST. After this rapid release of liquid water, the residual water can be collected via an evaporating-condensing process. Both the two water releasing processes can be powered by solar energy due to the existence of PPy-Cl with photothermal ability. This work provides insight into the synergetic effect of interpenetrated functional polymers and their potential for advanced AWH systems in the future. The controllable molecular water reservoir could be also established by the synergetic effect of a polymeric water trapper and a

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molecular solar heater. Porous sodium polyacrylate (PAAS)/graphene framework (PGF) is designed to capture moisture from common or smoggy environments and then release clean water with a high rejection rate of impurities under solar irradiation (Figure 8c).[69] Compared with single PAAS and PGF, the water uptake is greatly enhanced due to the synergistic effect arose from the microporous structure of PGF providing effective transport channels and an enlarged contact area for moisture (Figure 8d), leading to a high equilibrium uptake of 5.20 g_{water}/g_{PGF} at 100% RH. Besides, because of the excellent solar–thermal conversion property, the harvested water in PGF can be quickly released by using natural sunlight without other energy supply, and the produced water has a high quality which is free of impurities.

Despite the delightful progress, many ideas in this direction are still conceptual. Rational selection of components and incorporated functionalities is critically needed to develop superior moisture harvesters. For instance, utilizing hydrogels with high saturated water can enhance water uptake, and using environmental responsive polymer can directly release water in the liquid form. The ideal harvesting materials should have a porous structure for quick vapor diffusion during moisture capture, appropriate interaction with water for easy release, and a stable structure for long-term cycling stability. Structural expansion resulted from insertion of water molecules in the moisture-harvesting materials is able to lower water diffusion barriers along the molecular chains in the polymeric networks, but it may potentially deteriorate the stability of the whole structure. These issues require a delicate balance over high density of active regions for moisture capture and regionally selective water trapping without sacrificing the stability of materials. A trade-off between performance and stability is usually expected in this case, and extensive optimization may be needed. In addition, a deeper understanding of the underlying mechanisms on molecular water reservoir systems by means of advanced in situ characterization and theoretical modeling is also of great importance.

■ OUTLOOK AND OPPORTUNITIES

Being a geographically and climatically independent water production method, AWH technology is becoming more prominent for both emergency needs, such as disaster relief and decentralized water supply. Enabling moisture as a water resource could be considered as one of the most promising alternative strategies to overcome the challenges of long-distance potable water transport or delivery in rural areas. We have discussed the development track of AWH technology, and it is rather clear that material innovation is emerging as a potential direction to push forward such a technology. Sorbent materials can be utilized as moisture harvesters as long as the water affinity is tuned to enable the moisture concentration under low RH condition and water release upon low energy input. To this end, the design principles of moisture harvesters should be clarified (Figure. 9). First, the chemical stability toward moisture (water) is necessary to eliminate the contamination of obtained water. Second, the interaction between materials and water molecules should be strong enough to enable the operation at low RH or high-temperature conditions. Third, the concentrated moisture can be released by relatively small energy input. Forth, the microstructure of moisture harvesters should be tailored to allow airflow passing through at high flux. Fifth, the structural strength is required to be strong enough to maintain the designed structure during the water release.

Enabling moisture as a water resource could be considered as one of the most promising alternative strategies to overcome the challenges of long-distance potable water transport or delivery in rural areas.

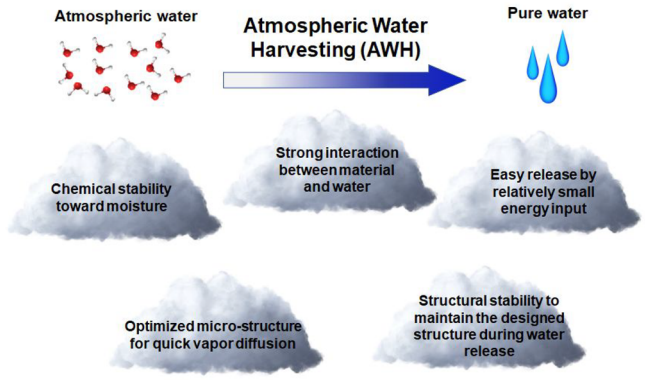

Figure 9. Outlook and perspective opportunities for next-generation AWH.

Along with the achievements so far, there are several key challenges to be overcome in further promoting AWH technology. The most significant challenge is to balance the requirement of moisture concentration and water release. An expansion of the operating regime of dewing can be achieved through the use of materials with strong water affinity to increase local moisture concentration. For most of water harvesters that exhibit good performance at low RH, the energy demand of water release is significantly greater than the condensation heat since a large amount of energy has to be consumed to re-vaporize the captured water for final collection. Consequently, extra energy input is required to power a heat pump operating at the Carnot limit for the heat dissipation during the condensation process. In this context, water release should be improved, which synergistically combines sorption and dewing processes to promote the AWH in a broader range of climates. In addition, architecting porous structures will enhance the exposure of AWH materials to moisture, facilitating the moisture capture. Controllable fabrication of highly ordered porous structures allows water management in the AWH material. Moreover, the AWH system, which is generally composed of moisture-harvesting materials, materials substrate and collection devices, can be optimized for efficient moisture concentration and water delivery.[25] For example, the interfacial heat and mass transfer resistances can be reduced by coating a thin layer of moisture-harvesting materials on substrates. By constructing micro-structures of the substrates, the vapor diffusion and water droplets migration could be improved, increasing the water production capacity. As such, tailoring system design corresponding to certain advanced AWH material is becoming an important strategy to explore the potential of the material. Efforts need to be taken to establish a standardized means to evaluate and select materials for AWH based on an optimized system with well-designed heat management, which can reveal

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the potential of new materials. Novel sorbent materials are critically needed to address such fundamental challenges. Both experimental exploration and theoretical prediction by computation simulations will be helpful in presenting a more in-depth insight into the migration and aggregation behaviors of water molecules during the AWH process.

The AWH technology is promising to be widely used for decentralized water supply in the future freshwater production market. Current water production techniques, such as multi-stage flash and multi-effect distillation, highly depend on complex infrastructure and need high energy consumption, leading to relatively high cost, and hence hindering their generalization in developing countries and remote regions. The materials enabled AWH is capable of producing water regardless of geographical and hydrologic conditions, and renewable energy can be utilized to avoid energy consumption by combusting traditional fossil fuel. Therefore, benefiting from the development of AWH materials, the cost of freshwater production will be reduced to an appealing level in the near future. In reflection of all aforementioned research efforts and promising prospects, moisture harvesters are able to expand the limits of current technologies and will significantly contribute to the alleviation of water scarcity.

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