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Water Harvesting from Air: Current Passive Approaches and Outlook

Xiaoyi Liu, Daniel Beysens,* and Tarik Bourouina*

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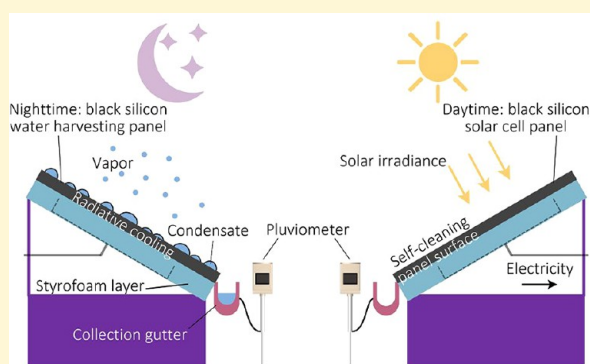
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ABSTRACT: In the context of global water scarcity, water vapor available in air is a non-negligible supplementary fresh water resource. Current and potential *energetically passive* procedures for improving atmospheric water harvesting (AWH) capabilities involve different strategies and dedicated materials, which are reviewed in this paper, from the perspective of morphology and wettability optimization, substrate cooling, and sorbent assistance. The advantages and limitations of different AWH strategies are respectively discussed, as well as their water harvesting performance. The various applications based on advanced AWH technologies are also demonstrated. A prospective concept of multifunctional water vapor harvesting panel based on promising cooling material, inspired by silicon-based solar energy panels, is finally proposed with a brief outlook of its advantages and challenges.



1. INTRODUCTION

Nowadays, four billion people are suffering from water scarcity and this trend is severely increasing globally.¹ Conventional fresh water access relies on rainfall, rivers, and lakes, with uneven distribution, depending on geographic location.^{2–5} Climate change, population growth, and water pollution issues have further exacerbated the imbalance of water resource distribution and difficulties of clean water access.^{6,7} Research efforts, although limited, has been devoted in the last decades to address this issue of water stress with various technologies, such as wastewater purification and seawater desalination.^{8–13} However, the utilization of these technologies are restricted by cost and water transportation capacity, especially for the undeveloped and landlocked regions.^{14,15} Most of other freshwater resources are contained within ice caps, glaciers, and deep groundwater, which are difficult to acquire. The global water reservoirs and their corresponding restrictions for acquirement and utilization are summarized in Figure 1. In this context, water vapor in the atmosphere, which has been ignored until fairly recently, can be seen as a feasible supplementary fresh water resource, because not only the atmosphere contains a large quantity of water vapor around $1.29 \times 10^{13} \text{ m}^3$,^{5,16} but also this water vapor is ubiquitous and it can be acquired without any restrictions of geographical and hydrologic conditions, being beneficial to household access to safe water without additional purification steps.^{17–19} Hence, to develop a globally accessible water resource, the reliable

approach of atmospheric water harvesting (AWH) is crucially desirable.

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efficient vapor condensation and liquid water collection, low energy consumption, less environmental and climatic limitations, good stability, and robustness.^{20–24} In accordance with these criteria, a large number of AWH technologies have been

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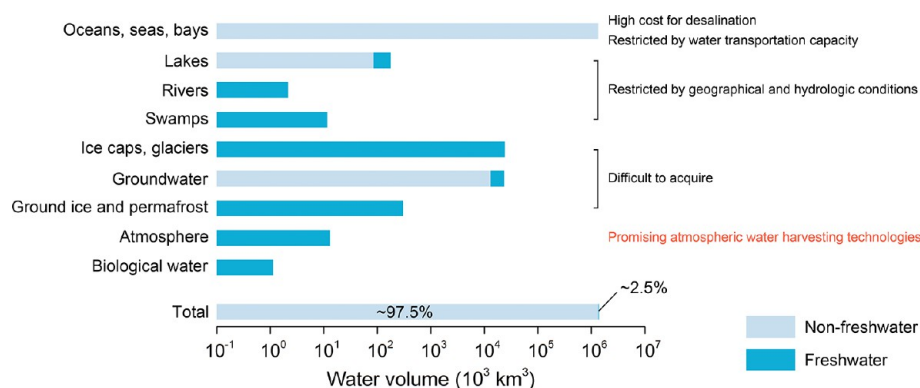


Figure 1. Global water reservoirs and their corresponding restrictions for acquirement and utilization.

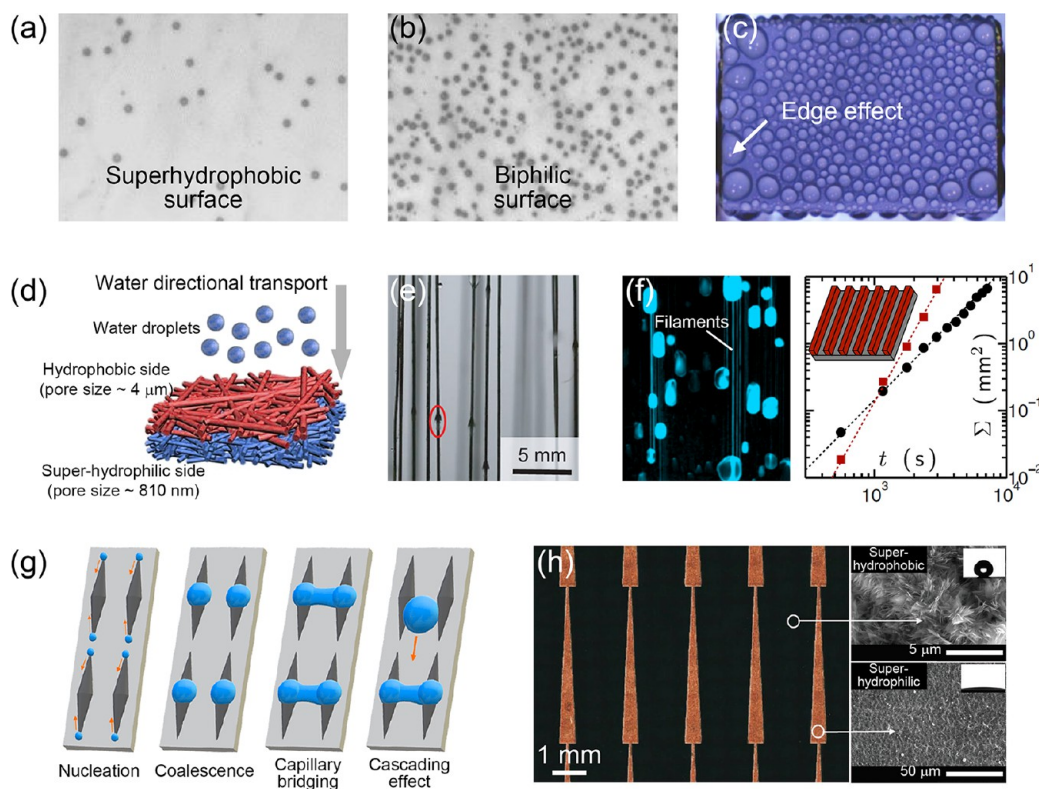


Figure 2. Studies on droplet nucleation, growth, transport and removal control. (a) Image of initial nucleation on a superhydrophobic surface. (b) Image of initial nucleation on a biphilic surface. [Reproduced with permission from ref 29. Copyright 2018, American Chemical Society, Washington, DC.] (c) Edge effect during condensation. [Reproduced with permission from ref 30. Copyright 2014, American Physical Society.] (d) Enhanced directional water transport capability achieved by Janus fibrous membrane consisting of hydrophobic/superhydrophilic layers. [Reproduced with permission from ref 33. Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.] (e) Fog harps. [Reproduced with permission from ref 34. Copyright 2020, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.] (f) Left: droplets and groove-filling filaments, marked by the fluorescent dye. Right: largest droplets sizes versus time on smooth and grooved surfaces, displayed in logarithmic scales. The inset is a schematic of grooved condenser surface. [Reproduced with permission from ref 35. Copyright 2019, American Physical Society.] (g) Schematic diagram of the cascading effect mechanism in water harvesting based on spindle patterns. [Reproduced with permission from ref 36. Copyright 2019, American Chemical Society, Washington, DC.] (h) Superhydrophilic and superhydrophobic hybrid patterns. [Reproduced with permission from ref 37. Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.]

developed involving either active or passive processes from an energy point-of-view. The active AWH systems usually possess excellent output water yield ranging from civil scale of 15–50 L d⁻¹ to industrial scale of 2000 L d⁻¹, but this is achieved at the expense of being driven by the electricity or other high-grade power supply.²³ The water yield of typical active devices, such as air-conditioning and condensing-coil integrated AWH systems and thermoelectric coolers, is related to the input power, which therefore leads to significantly large costs.²³

In contrast, one notes the appealing passive AWH processes, which do not require any energy demand or are completely driven by natural or sustainable power.²⁵ The conventional approaches are fog and dew collection on large-area nets or panels, whose water yield is normally modest and seriously influenced by environmental conditions.^{22–24} In addition, the heat released during the liquefaction process of droplets also has an adverse effect on the condensation of dew.²⁴ Various passive strategies have been accordingly developed in attempt to

improve the water harvesting capability, which can be roughly categorized into three types: (i) engineering new surfaces or materials for condensers to benefit dew generation and removal; (ii) cooling the condensing substrates to facilitate the dewing occurrence; and (iii) concentrating the moisture from air by sorbent-assisted systems to inhibit the environmental influences and raise the water yield. Fundamentally, these classes of passive strategies can be respectively seen as the modulation with respect to the three key factors during AWH processes, namely, interfacial dynamics, temperature, and relative humidity (RH). It is worth mentioning that those three modulation schemes can be intimately coordinated.

Although there are excellent recent papers with regard to either the exhaustive introduction of AWH schemes²² or more specific topics, such as one class of AWH systems categorized by specific configuration²⁶ or working principle,²⁷ less reviews are concerned with the approaches for improving AWH capability, that is water collection efficiency, especially when considering energetically passive approaches. Therefore, in this Review, we focus on the recent advances of passive AWH enhancement methods from the perspective of surface morphology and wettability optimization, substrate cooling, and sorbent assistance, respectively. We summarize their AWH performance, and give an in-depth analysis of their advantages and limitations. We also demonstrate a variety of applications developed on the basis of passive AWH strategies and propose realistic outlook accordingly, especially a new concept of multifunctional AWH panel based on promising new materials.

2. IMPROVING ATMOSPHERIC WATER HARVESTING CAPABILITY BY MORPHOLOGY AND WETTABILITY OPTIMIZATION

The purpose of engineering surface morphology and wettability is to promote the formation, growth, and shedding of the dew and consequently facilitate with the water harvesting capabilities by specific morphologies, properties or physical phenomena. It is a completely passive approach for AWH enhancement, which is accessible to not only the dew condensers but also the fog harvesters. Besides, the engineered surfaces can also be integrated into relatively more complicated AWH systems to achieve a better performance. The enhanced liquid water collection abilities are highly desirable, enabling the designed AWH systems to recover the light precipitations (radiative fog, drizzle) which are usually lost because pinned on the common collection substrates (e.g., roofs) and eventually evaporated back to the atmosphere. The fabrication cost and robustness are two key factors which must be taken into account in the surface design process, which enable it to be applicable to the large-area production and outdoor application. According to different mechanisms of action, the methods of morphology and wettability optimization can be categorized as the following types: (i) droplet nucleation and growth control, (ii) droplet transport and removal control, and (iii) aerodynamics control.

2.1. Droplet Nucleation and Growth Control. Dew condensation is the process of vapor–liquid phase transition on condensing surfaces. The first step of dew condensation is the formation of the smallest droplet nucleus, namely, nucleation.²⁸ The relatively high nucleation density is essential for efficient condensation. It has been noted that the nucleation density on hydrophilic surfaces is higher than that on hydrophobic surfaces, so the former is usually preferred as the nucleation sites when designing condensers. For instance, Figures 2a and 2b respectively show the images of initial nucleation on super-

hydrophobic surface and compound biphilic surface consisting of superhydrophobic substrate and hydrophilic nanosites.²⁹ The nucleation density on the biphilic surface can be controlled by tuning the hydrophilic site density, which allows a $\sim 349\%$ water collection rate as compared to the superhydrophobic surface.²⁹ Besides the nucleation, the droplet growth can also be controlled artificially. As shown in Figure 2c, the edge effects in condensation were apparently observed. It means that the droplets on the corners or edges can grow faster than others, since they can collect more vapor in the condensation process. In certain cases, it can even give the growth enhancement of droplets up to 500%.^{30,31}

2.2. Droplet Transport and Removal Control. In all the dropwise or filmwise condensation processes, water collection by gravity is revealed to be a common bottleneck problem.²⁸ Fast water transport and removal are highly needed to timely collect water and prevent its evaporation. Even if considering the active cooling by contact, the condensate should be rapidly removed to reduce as much as possible the thermal resistance of liquid water. Researchers therefore investigated various physical phenomena based on engineered dedicated microstructures and metasurfaces to achieve this objective. For instance, the modified mesh framework³² or fibrous material,³³ with the excellence of rapid fabrication capabilities, have been proposed to improve the water collection efficiency. A typical example is the hydrophobic/hydrophilic Janus fibrous membrane, which performs enhanced water harvesting capacity by virtue of its directional water transport mode, as shown in Figure 2d.³³ The water adsorption of the Janus membrane is facilitated by the enhanced directional wicking effect, forming between the larger pores in the hydrophobic side and the smaller pores in the superhydrophilic side, whose water harvesting capacity is 2.7–7 times higher than that of a single membrane;³³ water transport is also very important to fog harvesting. Figure 2e shows optimized fog harps, which can produce 5–78 times more water yield, compared with the common mesh fog net, because of its unobstructed drainage pathway.³⁴ More importantly, it can harvest appreciable fresh water amounts, even under light fog conditions, which is hardly achievable to the conventional fog net; in addition, by taking advantage of groove-filling imbibition phenomenon, tiny groove arrays with the width of $\sim 100\ \mu\text{m}$ and depth of $\sim 65\ \mu\text{m}$ have been adopted on the condenser surface to improve the dew harvesting capability. The droplets drained and merged mutually through the filaments in the grooves, leading to the acceleration of droplet growth, coalescence, and subsequent shedding from the surface, as shown in Figure 2f;³⁵ meanwhile, the shedding cascading effect has also been reported, based on spindle patterns.³⁶ On such specific surfaces, the small droplets were transported and mutually connected by the spindle bump, resulting in large droplets. Then, numerous small droplets can be passively removed by the sliding of larger droplets, hence reducing the loss induced by re-evaporation, as sketched for instance in Figure 2g.³⁶ The optimized patterns exhibited the water harvesting capability of $6.21\ \text{L m}^{-2}\ \text{h}^{-1}$, almost triple of that of the untreated surface;³⁶ additionally, another scheme of superhydrophobic–superhydrophilic hybrid metasurfaces with optimized triangle patterns has also been proposed, as shown in Figure 2h.³⁷ The two distinct surface nanomorphologies fabricated by laser ablation can simultaneously achieve fast droplet nucleation and growth on a superhydrophilic area, as well as directional water removal on a superhydrophobic area.³⁷ By exploiting the multiple coupling effects of the surface, an $\sim 21\%$ – 54% enhancement of dew harvesting capability was

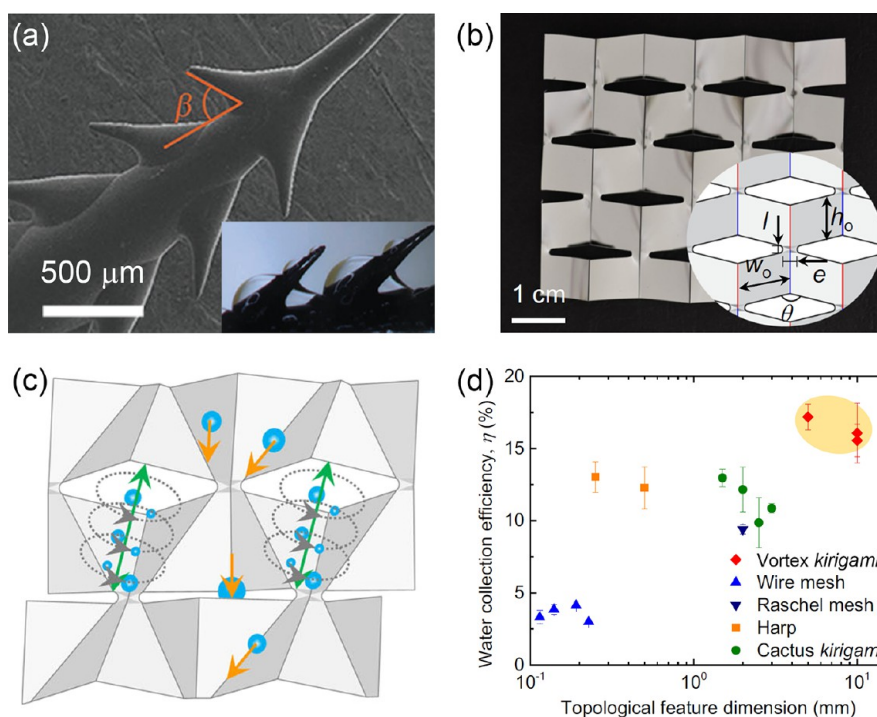


Figure 3. Studies on aerodynamics control. (a) Cactus-shaped fog harvesting microstructures. [Reproduced with permission from ref 50. Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.] (b) Schematic of vortex-based kirigami fog collector. (c) Schematic of the counter-rotating vortices and facilitated droplets ejection in the vortex-based kirigami. (d) Comparison of fog collection efficiencies of several fog collectors with their feature sizes. The collection efficiency is defined as the ratio of water collection rate to water delivery rate. [Reproduced with permission from ref 51. Copyright 2021 Springer Nature Limited.].

obtained compared with that of uniform superhydrophilic or superhydrophobic surface.³⁷ Besides these methods, researchers also obtained inspirations from natural insects and plants and designed structured surfaces to enhance the water harvesting capacity.^{38–42}

2.3. Aerodynamics Control. The collection by vertical nets of small condensed water droplets transported by winds in fog and clouds^{43–46} give interesting water yields, at most $\sim 10 \text{ L m}^{-2} \text{ d}^{-1}$,⁴⁶ but only specific foggy sites are favorable, some elevation above sea level being required in general. A research hot spot of fog harvesting is to design biomimetic structures inspired by desert beetle,⁴⁷ *tradesantia pallida*,⁴⁸ *Nepenthes*⁴⁹ and cactus⁵⁰ to increase the efficiency of atmospheric fog capture, which still acts by controlling the droplet transport and removal processes. Figure 3a presents the image of cactus-shaped fog harvesting microstructures.⁵⁰ Recently, Li et al. developed a new concept of fog collector acting through aerodynamics control.⁵¹ They proposed a centimetric kirigami structure to control the wind flow and then form counter-rotating vortices, which can facilitate the small droplets in the fog clusters to be ejected to the substrate (see Figures 3b and 3c). After structural optimization, such vortex-based kirigami fog collector can realize a water yield of $\sim 20\text{--}25 \text{ L m}^{-2} \text{ h}^{-1}$. Figure 3d presents a comparison of the fog collection efficiency of various fog collectors with their feature sizes.⁵¹ It is clear that, compared with other fog collectors, the vortex-based one achieved a higher efficiency, based on a relatively large topology size. Although fog harvesting is very convenient, its application is temporally and climatically restricted so as to be merely applicable to a few regions only. The mentioned different optimized surface morphologies and their effects on improving AWH capabilities are summarized in Table 1.

2.4. Analysis and Discussion. The collected water yield of optimized condensing surface can be as high as $67.6 \text{ L m}^{-2} \text{ h}^{-1}$ —measured with the assistance of a humidifier that is close to the condenser and directly provide the moisture for condensation.³³ Note that the natural dew condensers cannot be completely mimicked by such humidifier-assisted water harvesting setups, whose water yield is normally much larger than those of the former ones.^{33,36} On the other hand, fogwater collection rate varies obviously from site to site, but the average of common collectors is $\sim 3\text{--}10 \text{ L m}^{-2} \text{ day}^{-1}$.⁴⁶ The water yield can be increased by an order of magnitude with the assistance of aerodynamics.⁵¹ In general, passively harvesting water by condensers have relatively considerable water yield, but is dramatically limited by climate and RH conditions. Regardless of which condensation stage being regulated, they ultimately aim at collecting the generated water droplets as efficiently as possible by virtue of specific interfacial dynamics control, so as to avoid evaporation losses. However, the designed surface morphologies usually require not only precise or complicated fabrication process, such as magnetorheological drawing lithography⁵⁰ and laser ablation,³⁷ but a large contact area with air to improve the water yield. The manufacturing cost is therefore difficult to control. Considering that many fog harvesting projects are implemented in poor areas with scarce freshwater resources, the operation and maintenance of the equipment will be a main issue.⁴⁶ Additionally, from the fast water removal point-of-view, the proposed condensation schemes still have significant margin of progress.

Table 1. A Brief Summary of Several AWH Improvement Schemes Based on Surface Morphology and Wettability Optimization

physical phenomena involved	nucleation control ²⁹	edge effect ³⁰	directional wicking effect ³³	fog harps ³⁴	groove-filling inhibition phenomenon ³⁵	cascading effect ³⁶	fast droplet nucleation/growth and directional water transport ³⁷	aerodynamics control ⁵¹
optimized surface morphology	biphilic surface	several substrates with different surface roughness	hydrophobic/superhydrophilic Janus fibrous membrane	vertical wires	epoxy/SiO ₂ grooves	surface with spindle patterns	superhydrophobic–superhydrophilic patterned copper	kingami structure
features	large nucleation density	location-dependent droplet growth	directional water transport	unobstructed drainage pathway	accelerated droplet growth	large amount of passive droplet removal	fast water capturing and water removal	vortex wind flow
RH (%)	50 ± 2	44–78	NA ^a (droplets were generated by a humidifier)	NA ^a	50 ± 3	90 (moisture was provided by a humidifier)	50 ± 5	98 ± 1.7
subcooling (°C)	3 ± 0.5	9–17.8	NA ^a	NA ^a	29	NA ^a	24	NA ^a
water harvesting capability (L m ⁻² aerodynamics control h ⁻¹)	~0.5	NA ^a	67.6 ± 7.5	up to ~aerodynamics control 0.5 per day	~0.2	6.21	~1.1	~20–25
enhancement effect	~249% enhancement compared with superhydrophobic surface	up to ~500% droplet growth enhancement on edges or corners	170%–600% enhancement compared with single membrane	~400%–7700% enhancement compared with mesh fog collector	NA ^a	~40%–300% enhancement compared with untreated surface	~54% and ~21% enhancement compared with superhydrophobic or superhydrophilic surfaces	~150% enhancement compared with mesh fog collector
water removal onset time (min)	NA ^a	NA ^a	NA ^a	NA ^a	~25–80	<15	23–35	NA ^a

^aNA = not available.

3. IMPROVING ATMOSPHERIC WATER HARVESTING CAPABILITY BY SUBSTRATE COOLING

Generally, dew harvesting can be achieved from natural condensation,²⁸ with a maximum water yield of $\sim 1 \text{ L m}^{-2} \text{ d}^{-1}$, as limited by the available passive cooling power ($60\text{--}100 \text{ W m}^{-2}$) or from assisted condensation by forced cooling of a surface and its surroundings. Here, the energy yield for cooling, on the order of a few kW h L^{-1} ,²⁰ becomes limited by the available power. The feasibility of AWH through direct cooling condensation can be evaluated through the Moisture Harvesting Index (MHI), which is the ratio of condensation enthalpy to the total given heat.⁵² Obviously, the regions in the world with the higher content in water vapor, corresponding to hot and humid regions as the tropical areas, will require less energy yield for cooling.

In order to improve the AWH capability and directly obtain the dew, the active contact cooling devices based on thermal conversion and conduction such as Peltier cells are adopted in the vast majority of reported studies so far.^{30,35,37,53} In this process, a huge portion of input electrical energy is consumed for the purpose of cooling other components of surrounding air except vapor, leading to a relatively low efficiency.^{54,55} From the perspective of cooling efficiency, the sorbent-assisted vapor capture can be seen as a type of pretreatment of condensation that concentrates the vapor and makes the subsequent cooling and condensation more efficient. Accordingly, a regulation strategy of sorbent stepwise position was proposed by inducing an inner cooling source in the sorbent-assisted AWH system, which is able to improve its water harvesting capability with significantly reduced energy demand.⁵⁶

On the other hand, many researchers are not satisfied with this and are committed to research completely passive cooling technologies. The ultimate purposes of combining passive cooling into AWH strategies are (i) improving the yield of harvested water; (ii) avoiding or reducing the energy consumption in the cooling process; (iii) weakening the environmental restrictions and extend the applicable regions of the AWH approaches. In this part, we mainly introduce the utilizations of passive cooling in the field of AWH, especially the radiative cooling technology. The advantages and restrictions of several passive cooling approaches are also simply discussed.

3.1. Radiative Cooling for Atmospheric Water Harvesting. Radiative cooling is a process of losing heat by surface radiation through atmospheric transparency window ($8\text{--}14 \mu\text{m}$ spectral range),^{57–65} which is widely used in cooling various objects, such as buildings,^{66–69} solar cells,^{70–72} power plants,^{73,74} and even some liquids.^{75,76} It enables substrates to be cooled within a few degrees of each part, a value large enough to reach the dew point at night and condense water vapor in many areas of the world, including pwe,aaa and semiarid areas.^{28,77–80}

In the field of atmospheric vapor harvesting, radiative cooling is involved in a natural phenomenon, which is dew condensation, especially at night. Historically, the first documented report is the use of horizontal cloths by alchemists to condense dew.⁸¹ Dew water collected on polyethylene foil, which however presents a rather low emissivity, was then proposed in the middle of the 20th century to irrigate plants in arid areas.⁸² Low emissivity is nevertheless compensated to some extent by the large emissivity (0.98 in the atmospheric window) of condensing water.^{28,83,84} More recently, a specially made foil (usually called “OPUR foil”) comprised of low-density

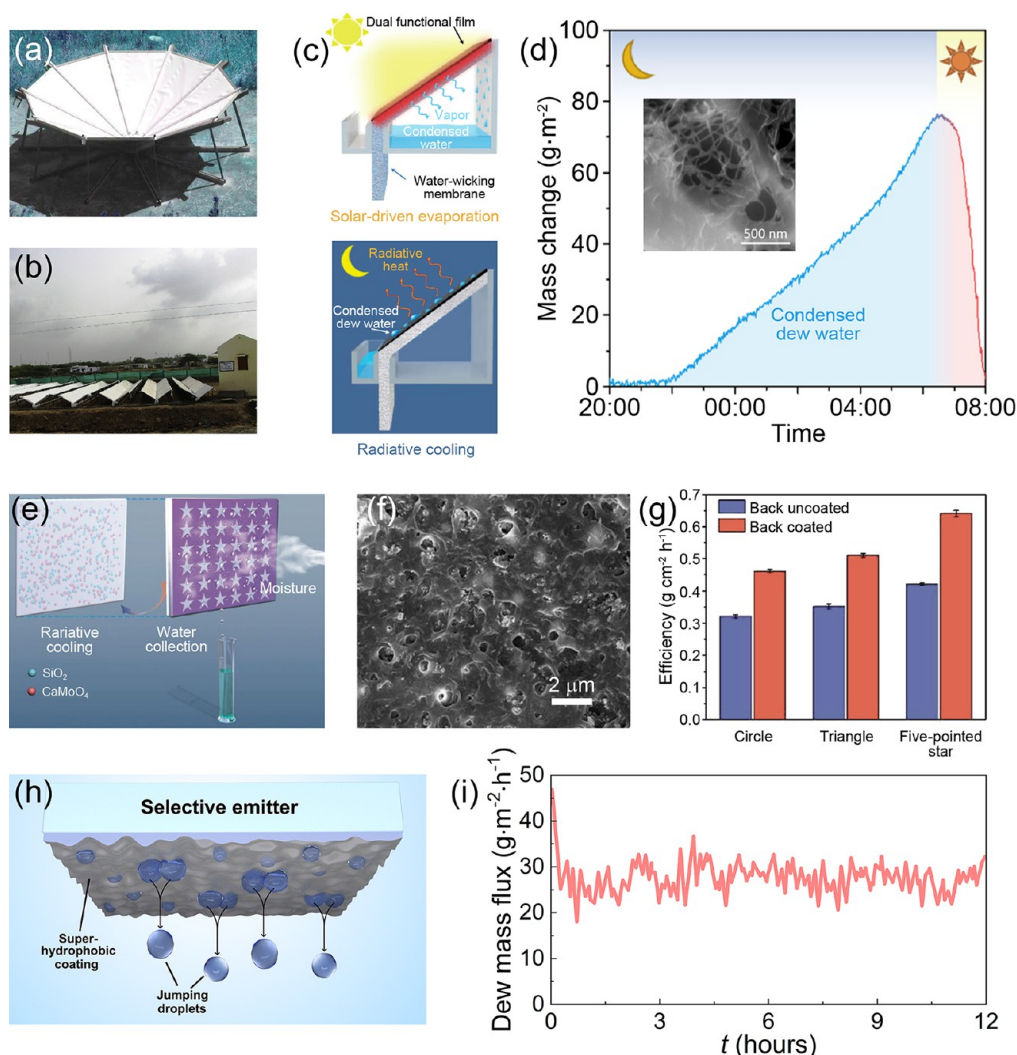


Figure 4. Examples of embedding radiative cooling technologies into AWH strategies: (a) funnel-shaped dew condenser covered with OPUR foil. [Reproduced with permission from ref 86. Copyright 2009, Elsevier BV] and (b) dew plant. [Reproduced with permission from ref 93. Copyright 2016, Elsevier, Ltd.] (c) Schematic of AWH system with a dual functional film, which can vaporize the wicked saline water for desalination by absorbing the solar energy at daytime, and passively cool the condenser surface for dew formation and collection at nighttime. (d) The harvested dew mass during a night. The inset presents the SEM image of the porous microstructure on the dual functional film. [Reproduced with permission from ref 94. Copyright 2020, American Chemical Society, Washington, DC.] (e) Schematic of an AWH condenser with a patterned facade and a radiative cooling backside. (f) SEM image of radiative cooling surface containing SiO₂ and CaMoO₄ nanoparticles. (g) Water harvesting efficiencies of samples with and without radiative cooling coating under different facade patterns. [Reproduced with permission from ref 95. Copyright 2020, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.] (h) Schematic of the jumping-driven droplet detachment from the superhydrophobic condensing surface presented in ref 96. (i) Dew mass flux rate of the proposed AWH system measured in 12 h. The data have been extracted from ref 96.

polyethylene film with embedded TiO₂ and BaSO₄ microspheres and food-proof, water-insoluble surfactant was developed^{85–88} to serve as a cooling and droplet-collecting surface to be placed on a thermal-insulated Styrofoam plate. A relatively high infrared emissivity (~ 0.94 , close to the condensing water emissivity) of this foil guarantees the cooling effect at night, while its white color delays to a certain extent the condenser warming in the daytime, because of the high reflectivity in the visible solar spectrum range. The performance of dew condensers is also subject to their frameworks and shapes.^{28,86} Figure 4a displays a typical funnel-shaped dew condenser covered with OPUR foil.⁸⁶ In addition to the enhanced gravity-driven collection of the condensed dew water, such funnel framework can prevent the heating effect of wind, reducing the thermal convection and collecting the cold heavy

air inside the funnel space. Inclined plane condensing panel is another commonly used dew condenser.^{28,87,88} Large-area prototypes of foil panel,^{89,90} and even dew plants (see Figure 4b),^{91–93} have already been implemented to validate the feasibility of nocturnal dew generation promoted by radiative cooling, even under wind speeds as large as 4.5 m s⁻¹.²⁸ Compared with an ordinary condensing panel, the yield of dew water obtained from the improved one was indeed increased by up to 20%.⁸⁸ Generally, this class of dew foils emphasize on the advantages brought by their optical characteristics rather than the wetting characteristics.

Besides the polyethylene-based foil, several materials with high infrared emissivity are also developed to work as the component of other AWH devices. Xu et al. deposited multiwalled carbon nanotubes on a flexible substrate (e.g.,

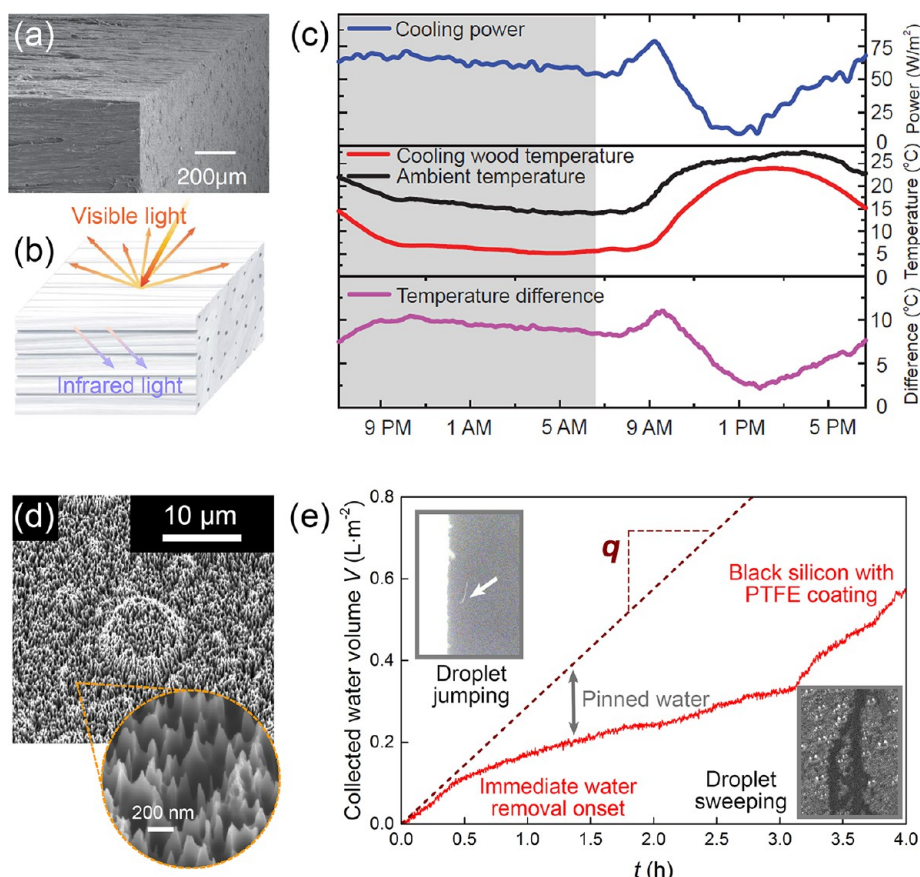


Figure 5. Promising condensing materials with optimized morphology and unique properties regarding both wetting and radiative cooling abilities. (a) SEM image of the cellulose fibers and channels of the magic wood. (b) Schematic of the magic wood with strong scattering of visible light and strong absorption of infrared light. (c) Cooling effect of the magic wood versus time. [Reproduced with permission from ref 97. Copyright 2019, American Association for the Advancement of Science.] (d) SEM image of needle-shaped black silicon surface with high aspect ratio. (e) Water harvesting capacity of the modified black silicon versus time. Left and right insets are photographs of the droplet jumping and sweeping motion modes, respectively. [Reproduced with permission from ref 119. Copyright 2021, Cell Press.]

polycarbonate, acrylonitrile butadiene styrene, or printing paper) to manufacture a dual functional film for water desalination at daytime and dew collection at night, as shown in Figure 4c.⁹⁴ The desalination is driven by solar energy with the $\sim 95\%$ solar irradiance absorptivity, while the ~ 0.9 emissivity in atmospheric window achieves the passive radiative cooling and the promoted dew generation, leading to a dew harvesting capability of $\sim 0.1 \text{ L m}^{-2} \text{ d}^{-1}$ at night, as shown in Figure 4d.⁹⁴ Distinct from the high solar reflectivity for common radiative coolers, herein the great absorptivity is maintained to integrate unexpected functions into the AWH system.

On the other hand, the passive substrate cooling by radiation and surface morphology optimization can be conducted simultaneously. Embedding SiO_2 and CaMoO_4 nanoparticles in the polymer matrix can produce a passive cooling thin film.⁹⁵ A combined condenser is accordingly designed containing such film as the backside, and a microstructured aluminum surface with star patterns as the facade, as shown in Figure 4e. Figure 4f displays the SEM image of the surface morphology of the composite coating, while Figure 4g gives the comparisons of water harvesting capabilities between coated or uncoated samples with different facade patterns. According to Figure 4g, the enhancement of AWH capacity induced by the radiative cooling effect is obvious. Not only the functional back layer enables a theoretical cooling effect of $18 \text{ }^\circ\text{C}$, but it also neutralizes the heat released by droplets condensation and

facilitates the subsequent nucleation, ultimately increasing the water harvesting capability by 43%–52%, even up to $\sim 6.3 \text{ L m}^{-2} \text{ h}^{-1}$.⁹⁵

Recently, an ingenious AWH prototype has been proposed, which synergistically combines radiative shielding and cooling effects with an engineered superhydrophobic condensing surface.⁹⁶ A multilayer selective emitter plays a key role, together with a radiation shield, which is able to not only resist sunlight and atmospheric radiative heat, but also radiate the latent heat of condensation to outer space, leading to an uninterrupted 24-h AWH performance. Meanwhile, a superhydrophobic thin coating with hierarchical microstructures is adopted as the condensing surface, enabling the condensate to spontaneously detach from surface by droplet coalescence and jumping behaviors. Figure 4h is a schematic of the jumping-driven droplet detachment from the superhydrophobic surface. A remarkable water harvesting capacity of $0.028 \text{ L m}^{-2} \text{ h}^{-1}$ is realized according to the dew mass flux test of the proposed rational AWH system given by Figure 4i. The simultaneous temperature and morphology modulation allows at least double yield of the state of the art, furthermore being achieved by a completely passive manner.⁹⁶

In particular, here we would like to briefly introduce two promising materials that may serve as a morphology-optimized condenser simultaneously assisted by a radiative cooling effect. In other terms, those materials have both wetting and optical

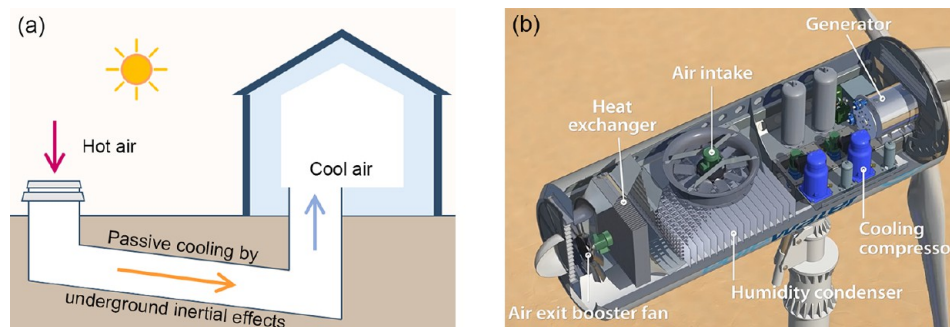


Figure 6. Potential passive cooling manners in AWH strategies, including (a) Canadian Wells, enabling the air to be cooled by underground inertial effects, and (b) wind turbines, which can produce considerable condensate water merely driven by wind power. [Reproduced with permission from ref 23. Copyright 2020, Oxford University Press.]

properties that fit with the requirements for efficient harvesting of dew water by passive cooling. The first candidate, magic wood, is a type of artificially processed wood obtained from natural wood through complete delignification and subsequent mechanical pressing.⁹⁷ Such novel material consists of multiscale cellulose fibers or fiber channels (see Figure 5a), which can potentially act as the grooves during condensation and trigger groove-filling imbibition phenomenon to accelerate the growth and shedding of dew droplets.³⁵ Meanwhile, the magic wood presents intense scattering in the visible range and consequent weak absorption for solar energy, because of the cellulose fibers, as well as strong emission in infrared wavebands attributed to the stretching and molecular vibration of cellulose (see Figure 5b), enabling the all-day radiative cooling effect to be effectively achieved. Figure 5c displays the cooling power and cooling effect of the magic wood versus time. An ~ 10 °C temperature decrease is observed at night, which is predictably capable of promoting the water harvesting efficiency when the magic wood serves as a condenser. More importantly, the magic wood possesses a mechanical strength of more than 400 megapascals, eight times higher than that of natural wood, which may provide excellent robustness, being applicable for large-area processing.⁹⁷

The second candidate, black silicon, is a type of unique material with needle-shaped surface structures and high aspect ratio, as shown in Figure 5d. It can be fabricated by femtosecond laser irradiation^{98–107} or physical/chemical etching.^{108–111} After appropriate surface modification, the needle-shaped morphology results in the “truly superhydrophobic” surfaces,^{112–118} which allows not only a large contact angle ($>150^\circ$) but also a small contact angle hysteresis (the difference between advancing and receding contact angles). The condensed droplets can easily detach from such a surface through sweeping or jumping.¹¹⁹ The former is caused by the droplet in-plane coalescence and the neighboring droplets along sweeping motion track will be taken away by the shedding large droplet, resulting in remarkably fast water removal and surface refreshing abilities.¹²⁰ The latter is induced by the droplets out-of-plane coalescence,^{121–127} which occurs at the very early stage of condensation and assists the removal of small droplets, contributing to the water collection and the reduction of evaporative loss.¹²⁸ Figure 5e displays the excellent water harvesting capacity and very fast droplet removal of the reported black silicon.¹¹⁹ On the other hand, by virtue of the combined effect of surface topography and dopant elements, black silicon is also able to achieve ultrabroadband absorption enhancement even exceeding 90% in the atmospheric window, leading to the potential radiative cooling ability.¹⁰⁵ Note that the practical

emissivity of black silicon during condensation can be further increased compared with that of the dry one, since the condensed water on the surface possesses large emissivity of 0.98 in atmospheric window, by which the infrared emissivity of black silicon can be compensated.^{28,83,84}

3.2. Other Passive Cooling Approaches for Atmospheric Water Harvesting.

3.2.1. Canadian Wells.

When discussing passive substrate cooling strategies except radiation cooling, one should mention first the inertial condensation that occurs in the well-known Canadian Wells^{129,130} commonly used for passively cooling dwellings. It uses the fact that, at some depth in the ground, the temperature in spring and summer is cooler than the surface temperature, because of inertial effects (see Figure 6a).¹³⁰ The delay time at a few meters from the ground surface can be on the order of several months and thus allow temperatures below the air dew point to be maintained precisely during the hot, summer seasons. Humid air ventilated from the surface will thus lead to condensation to occur in the cool region. Several investigations have been performed in the beginning and middle of the last century.^{131–133} More recent theoretical studies are dedicated to this effect.¹²⁹

3.2.2. Wind Turbines.

In addition, some integrated atmospheric vapor condensing systems can be completely driven by passive natural or sustainable sources of energy. For instance, Figure 6b displays the internal structure of a commercial wind turbines, which have already been developed and contained a cooling compressor driven by wind energy. The output power of such integrated system is ~ 30 kW and the produced water yield is ~ 1000 L d^{-1} , without any extra energy demand except wind energy.^{23,134} Generally, the water yield of such system will be related to the dependent natural or sustainable energy source, whose efficiency and stability are the major concerns for evaluating its performance.

3.3. Analysis and Discussion.

The nature of improving AWH capability by passive cooling is to trigger and promote dew condensation by temperature modulation. Meanwhile, it also reduces the required RH for dew condensation and expands the applicable geographical regions of condensation-based AWH over the world. For the AWH system assisted by radiative cooling, although the dew yield is limited by the available radiative cooling power, the fact that energy is free, clean, zero-carbon, and the devices are robust enough to work even if partially damaged, makes this technology particularly attractive. The manufacturing costs of radiative cooling devices are also relatively low since such materials do not require complex morphologies or structures. Note that the effect of radiative cooling will be severely weakened by the thermal conduction

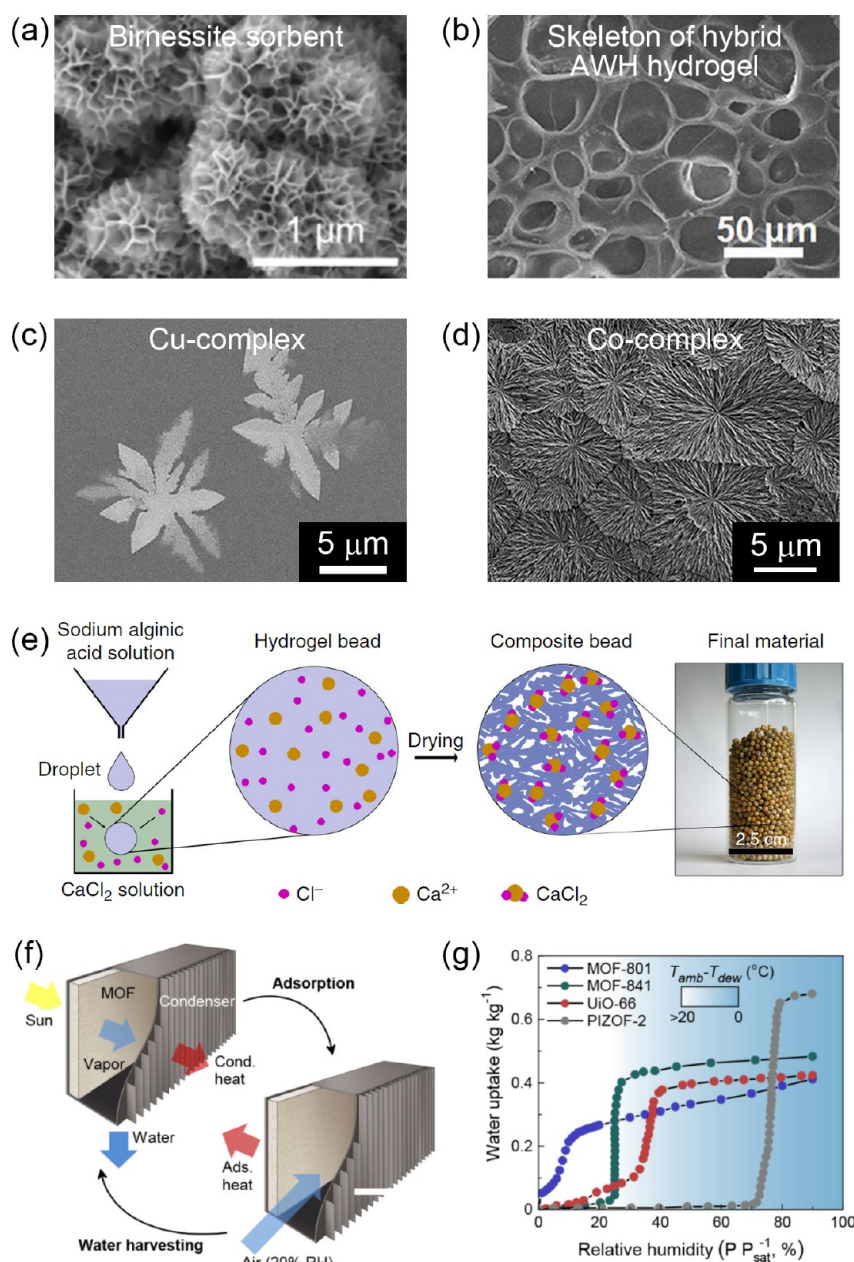


Figure 7. Examples of common desiccant materials, composites and MOFs adopted in passive indirect AWH systems. (a) SEM image of layered birnessite MnO₂ structure. [Reproduced with permission from ref 165. Copyright 2019, American Chemical Society, Washington, DC.] (b) SEM image of hybrid skeleton-shaped hydrogel consisting of hygroscopic polymer and hydrophilic gel. [Reproduced with permission from ref 167. Copyright 2019, Wiley–VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.] (c) SEM image of Cu-complex. [Reproduced with permission from ref 168. Copyright 2020, Wiley–VCH GmbH.] (d) SEM image of Co-based super hygroscopic complex. [Reproduced with permission from ref 169. Copyright 2021, Wiley–VCH GmbH.] (e) Schematic of the production process for the composite beads consisting of alginate-derived matrix and embedded calcium chloride. [Reproduced with permission from ref 175. Copyright 2018, Springer Nature, Limited.] (f) Schematic of MOF-801-based AWH system prototype. (g) Water adsorption isotherms for several Zr-based MOFs, including MOF-801. [Reproduced with permission from ref 185. Copyright 2017, American Association for the Advancement of Science.]

and convection between substrate and air, thus it is desirable to set up a windshield around the radiative cooling component, or use it together with other AWH systems.¹³⁵

Scientists have been looking for promising materials that can serve as a morphology-optimized condenser and simultaneously be cooled by radiation. Predictably, qualified candidates must satisfy some prerequisites. Concretely, it not only requires the high emissivity or absorptivity in the atmospheric window waveband to achieve radiative cooling, but also an engineered slippery surface to efficiently collect the water condensate.²²

Both properties have in common the characteristics of special requirements for surface morphology. From this perspective, some common radiative cooling materials, including flat multilayer film configuration,^{64,65,136–141} polymer-based metamaterials,^{142–148} and textiles^{149,150} are not suitable for water collection. On the other hand, some radiative cooling metasurfaces with complicated patterns are also undesirable for harvesting water, since their high cost and complex fabrication processes will, to a certain extent, impede the large-area production.

Canadian Wells provide an environment or location rather than new materials for achieving passive cooling. Therefore, it possesses excellent compatibility since other AWH systems can be placed in it and work at a lower temperature when the tube is large enough. Canadian Wells are suitable for irrigation and domestic water harvesting, but only the residents living in individual houses or low-rise of the building can directly benefit from them. The construction program of Canadian Wells also needs to be planned well prior to building construction. On the other hand, wind turbines are a type of relatively complete AWH system, which can provide considerable output power and water yield. A single turbine can generate enough water for a village of 2000–3000 residents. However, the installation cost of single turbine is \$660 000–\$790 000, which is the main issue preventing it from being put into use.¹³⁴ Note that wind is unfavorable for radiative cooling, but is beneficial to the AWH in Canadian Wells¹²⁹ and turbines. Wind power is even the basis for the operation of the latter. Therefore, the effect of wind cannot be generalized for these passive cooling methods, which should also be taken into account besides temperature and relative humidity (RH).

4. IMPROVING AWH CAPABILITY BY SORBENT ASSISTANCE

As known, the relative humidity (RH) is one of the most critical factors affecting the performance of vapor harvesting.^{20,21} It entirely depends on the local climate and is difficult to control artificially. A general limitation in the yield of water/energy in condensation as measured by the MHI (see above) is the necessity to cool the moist air while only water vapor will be condensed. Therefore, attempts using selective membrane technology have been made as the pretreatment of dew condensation to extract water molecules from air in order to increase the condensation yield.^{54,55} The use of membranes is an interesting endeavor that should indeed enhance the condensation yield, which however usually needs pumps to impose a concentration gradient.^{54,55} Another option to modulate RH before condensation is to use the sorption–desorption cycle.^{151–153} This type of vapor harvesting strategies work with the assistance of sorbent materials during vapor capture, while the harvested water need to be desorbed subsequently, usually under relatively high temperature so as to overcome the affinity of sorbents toward water.^{154,155} Besides good water harvesting capacity, the relatively low temperature for water regeneration is another target for designing and preparing promising sorbent materials, even allowing the harvested water being desorbed by passive manners.^{154,155} Note that, in this case, not only surface effects must be considered; the volume also matters, especially when dealing with porous materials; the corresponding weight unit is usually referenced in terms of kg_{sorb} . The common sorbents and their corresponding passive water desorption processes are introduced as follows.

4.1. Sorbents for Water Sorption. **4.1.1. Desiccant Materials.** Desiccants are usually adopted as the bed substrate in the designed AWH systems with a chamber for water desorption and subsequent condensation.²¹ Common desiccant materials include hygroscopic salts,^{156,157} silica gels,^{158–162} zeolites,^{163,164} birnessites,¹⁶⁵ hydrogels,^{166,167} metal complexes,^{168,169} etc. The first three are commonly seen, inexpensive desiccant materials which have been frequently reported and reviewed.^{21,154,155} They can provide moderate water harvesting efficiency with relatively difficult desorption process. Nevertheless, some distinguished desiccants among them are capable

of harvesting moisture at a relatively low RH and releasing harvested water merely by sunlight irradiation.^{157,159–162,164} Figure 7a displays a different desiccant material: birnessite MnO_2 . The water sorption capacity of layered birnessite is ascribed to the hydration characteristics of interlayer ions and proper layer spacing.¹⁶⁵ Meanwhile, it possesses great optical absorptivity in solar spectrum, which is beneficial to increase its temperature and trigger the occurrence of interlayer water desorption by solar irradiation;¹⁶⁵ various hydrogels can also be used as sorbent materials such as superhygroscopic fringed structure comprised of Zn and O,¹⁶⁶ and hybrid skeleton-shaped network of hygroscopic polymer and hydrophilic gel (see Figure 7b).¹⁶⁷ The maximum water yield of former Zn–O hydrogel is over $10 \text{ L kg}_{\text{sorb}}^{-1} \text{ d}^{-1}$, which is an order of magnitude greater than that of silica gel.¹⁶⁶ The latter hybrid hydrogel exhibits higher water harvesting capability, even more than $50 \text{ L kg}_{\text{sorb}}$ per d^{-1} at RH = 90%.¹⁶⁷ More importantly, the water desorption of these hydrogels can be conducted at fairly low temperatures (down to $\sim 50 \text{ }^\circ\text{C}$), which is accessible by solar heating;^{166,167} metal complexes are also developed as promising atmospheric water sorbents.^{168,169} By virtue of a novel Cu-complex material (see Figure 7c), Yang et al. developed an automated and self-sustainable SmartFarm irrigation system with a water sorption capacity of up to $3.0 \text{ L/kg}_{\text{sorb}}$ at RH of 95%.¹⁶⁸ Another metal complex—cobalt-based superhygroscopic complex—is presented in Figure 7d. The saturated water uptake of such Co-complex is $\sim 4.64 \text{ L kg}_{\text{sorb}}$ also at RH = 95%.¹⁶⁹ The water desorption of both Cu- and Co-complex can occur at temperatures as low as $\sim 60 \text{ }^\circ\text{C}$, which can be totally realized by solar irradiation. Even if connecting them to active systems to achieve some advanced functions, the energy consumption is very low.¹⁶⁹

4.1.2. Composites of Matrix Hosts and Salts. In order to further improve the water harvesting capacity, the investigations on composites combining matrix hosts materials and salts recently have become a research hotspot.^{170–175} Researchers attempt to respectively take advantage of the hygroscopicity and other remarkable properties of the host components to acquire excellent performance that cannot be realized by single desiccants. In some classic examples, several unique silica gels, alumina and porous carbon materials have been designed to be the hosts, while the calcium chloride or lithium bromide are adopted as the hygroscopic salts.¹⁷⁰ The investigations using large pore crystalline structures (MCM-41)¹⁷¹ and active carbon felt¹⁷² as the matrix hosts have also been reported. The relatively low working temperature for releasing harvested water of mentioned composites above makes them possibly passive and energy-efficient. Besides the traditional host materials, some distinguished hydrogels are recently developed as the matrix materials. For instance, Li et al. has proposed a type of sorbent by embedding the deliquescent CaCl_2 solution into the cross-linked hydrogel.¹⁷³ The former is responsible for harvesting water from atmosphere and the latter involves a flexible hydrogel network that enhances the water sorption capacities, because of the easily expandable pores. It is worth mentioning that the entire material will maintain solid state after absorbing water. The assembled AWH device with such a composite is capable of providing a water yield of 3 L d^{-1} at RH = 60%, merely with an evaluated cost of \$1.76.¹⁷³ In another example, the binary polymer salt is used in combination with functionalized multiwalled carbon nanotubes embedded in the hydrogel structure. The composite presents high water affinity to harvest vapor, while the carbon nanotubes not only serve as the

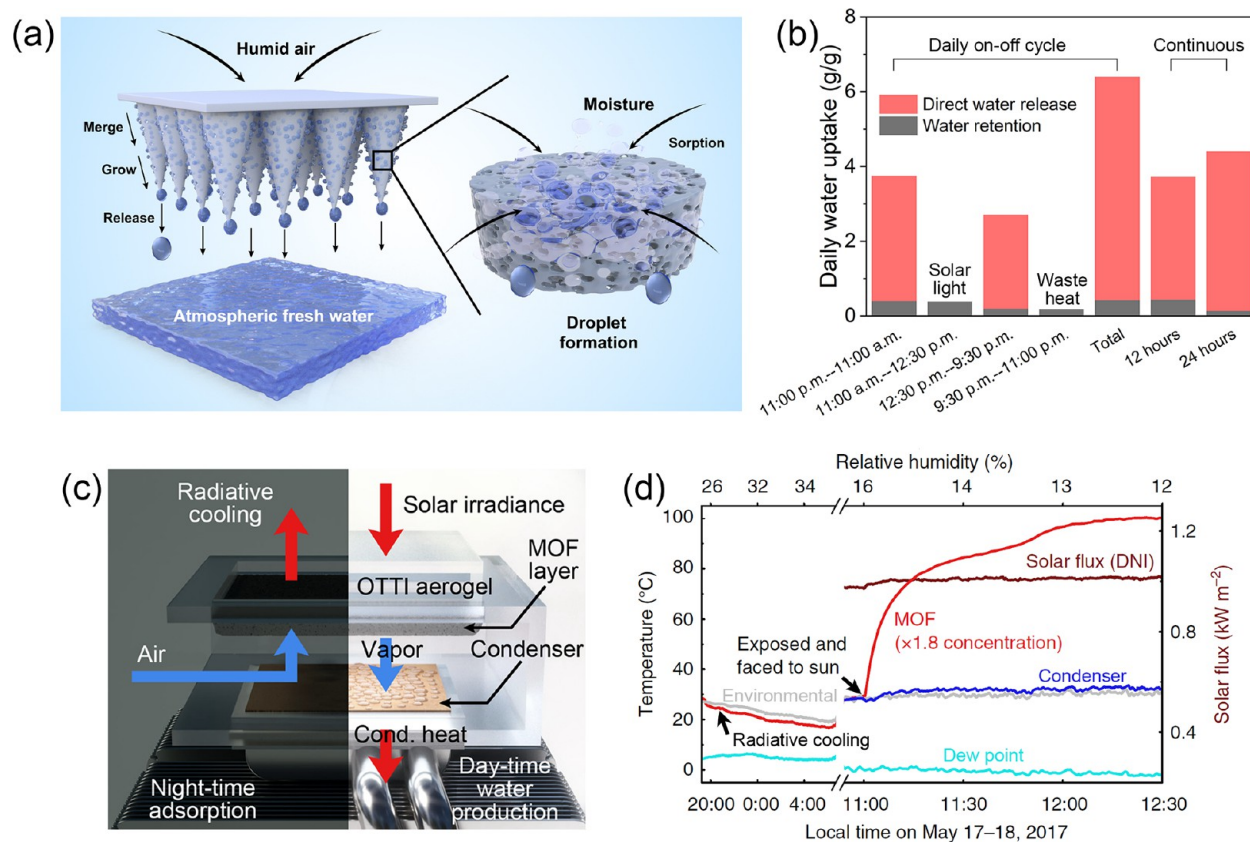


Figure 8. Radiative cooling-assisted MOF system. (a) Schematic of the polymer-MOF matrix inverted cones array presented in ref 193. (b) Comparison of daily water uptake between normal on–off cycle mode and continuous mode. The data is extracted from ref 193. (c) Schematic of the AWH system which can adsorb vapor at night, assisted by radiative cooling and desorb harvested water during the day, driven by solar energy. (d) Representative temperature profiles of MOF layer, condenser, environment, dew point, and solar flux versus time, with the 1.8× incidence concentration. [Reproduced with permission from ref 194. Copyright 2018, Springer Nature, Limited.]

mechanical support for the network structure, but also enhance the solar light absorption and increase the surface temperature up to 80 °C for water desorption. The AWH prototype containing such composites can conduct several cycles of water harvesting per day with the water sorption efficiency of 1–6 L kg_{sorb}⁻¹ in each cycle.¹⁷⁴ Figure 7e displays the production scheme for the third example, namely, the composite beads consisting of alginate-derived matrix and embedded calcium chloride.¹⁷⁵ In CaCl₂ solution, the dripping alginate solution will form spherical hydrogel droplets containing the incorporated Ca⁺ and Cl⁻ ions, and ultimately form the composite beads after drying. The involved materials in synthetic route are inexpensive and nontoxic, allowing for mass production. Under a water vapor pressure of 10 mbar, one cubic centimeter of such composite beads can absorb 0.66 g of atmospheric water which can be mostly released at 100 °C, accessible to be driven by solar heating.¹⁷⁵ Most importantly, the mentioned composite AWH materials are able to work in broad ranges of RH, even lower than 20%, potentially being applicable to the arid regions in the globe.^{172–175}

4.1.3. Metal–Organic Framework (MOF). MOFs are listed separately since they recently became one of the most attractive classes of vapor sorbent materials that consist of secondary building units (SBUs) linked by organic molecules.^{26,176–189} Figure 7f displays a schematic of a classic AWH system consisting of a MOF layer for vapor capture and a condenser for the released water condensation and collection.¹⁸⁵ The MOF layer adopted here is a typical architecture, namely, MOF-801,

with the molecular structure of [Zr₆O₄(OH)₄(-CO₂)₁₂]. Such AWH device can be completely powered by solar irradiation without any additional energy input. Figure 7g gives the water adsorption response for several Zr-based MOFs when varying the environmental conditions. Compared with other water harvesters, the water capture of MOF-801 can be rapidly triggered from a surprisingly low RH of ~8%. When RH reaches 20%, its water harvesting capability increases up to more than 0.25 L kg_{sorb}⁻¹ through a temperature swing between 25 °C and 65 °C.¹⁸⁵ It indicates that MOF-801 is able to implement a daily water yield of 2.8 L kg_{sorb}⁻¹ at quite low RH conditions, which is sufficient for either drinking or irrigation demands in severely arid areas.¹⁸⁵ Besides MOF-801, numerous SBUs and link molecules have been utilized to construct various MOFs, consequently resulting in a wide variety of framework topologies.^{26,186–189} The novel MOF-based atmospheric water harvester with the ability of multiple water harvesting cycles per day has also been developed, which is able to rapidly finish the water adsorption–desorption process within minutes, and merely powered by solar electricity.¹⁹⁰ On the other hand, similar to the composite hydrogels, the MOF matrix can be modified by other sorbent materials as well, such as hygroscopic salt¹⁹¹ and polymer.^{192,193} The former realizes an enhanced water sorption capacity of 0.77 L kg_{sorb}⁻¹ at RH = 30% and an energy-free desorption merely driven by natural sunlight.¹⁹¹ The latter has more diverse functions. Karmakar et al. demonstrated a composite in which the MOF wrapped around a polymer component.¹⁹² It has the phase transition ability between

Table 2. Key Parameters of Water Sorption and Desorption Kinetics of Mentioned Sorbent Materials, As Well As Their Highlighted Features

material	ref source	water uptake, L kg ⁻¹ _{sorb} (temp, RH)	desorption temp (°C)	features
birnessite MnO ₂	165	0.19 (25 °C, 75%)	85	excellent solar absorptivity of birnessite
Zn–O hydrogel	166	4.5 (25 °C, 90%)	50	water harvesting from humid air above sea surface
hygroscopic polymer and hydrophilic gel	167	6.8 (~25 °C, 90%)	42	excellent water uptake
Cu-complex	168	3 (20–40 °C, 95%)	60	applied in automated and self-sustainable Smart-Farm irrigation device
cobalt-based complex	169	4.64 (25 °C, 95%)	55	applied in machine-learning-assisted autonomous humidity management system
MCM-41 with CaCl ₂	171	1.75 (10–15 °C, 78%–92%)	80	applied in portable solar-driven water production prototype
active carbon felt with LiCl	172	1.2 (25 °C, 90%)	77	strong water sorption ability in low RH condition
cross-linked hydrogel with CaCl ₂	173	1.75 (25 °C, 80%)	60	low cost for water production
alginate hydrogel with binary salts	174	5.6 (25 °C, 90%)	70	excellent water sorption capacity with a high photothermal conversion efficiency
alginate-based matrix with CaCl ₂	175	1 (28 °C, 26%)	100	using cheap, nontoxic, and easily accessible materials in synthetic route
MOF-801	185	0.4 (25 °C, 90%)	65	strong water sorption ability in low RH condition
MIL-101(Cr) with LiCl	191	0.77 (30 °C, 30%)	85	strong water sorption ability in low RH condition
MIL-101(Cr) with thermoresponsive polymer	192	4.4 (25 °C, 96%)	40	temperature-triggered water capture and release behavior
polymer-MOF mixed-matrix	193	3.75 per day (25 °C, 90%)	ambient	as by engineered morphology for continuous water sorption and desorption without energy input
MOF-801 with OTTI aerogel	194	0.275 (15–25 °C, 40%)	75	assisted by radiative cooling

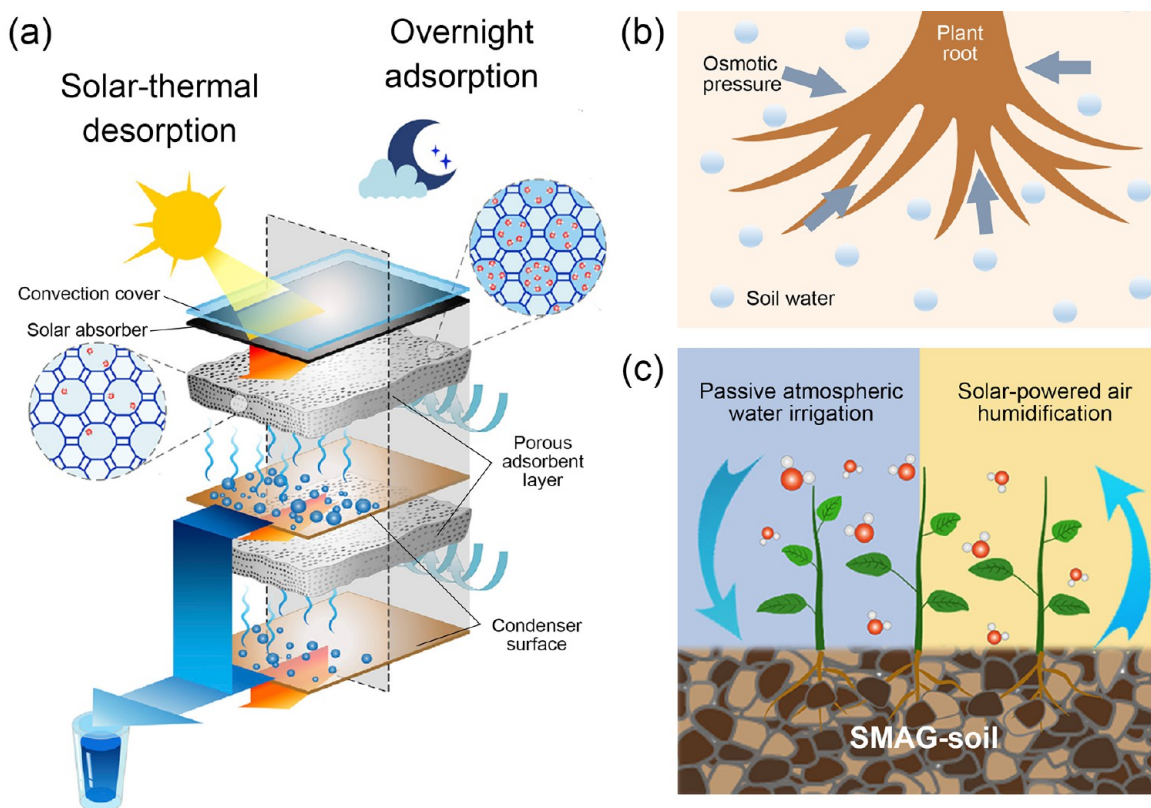


Figure 9. Commonly seen passive water desorption strategies. (a) Schematic of the dual-stage AWH system. [Reproduced with permission from ref 196. Copyright 2020, Elsevier, Inc.] (b) Schematic of osmotic mechanical pressure which can help extracting water from soil and provide water to the plant roots. (c) Schematic of the atmospheric water irrigation based on SMAG-soil. [Reproduced with permission from ref 201. Copyright 2020, American Chemical Society, Washington, DC.]

hydrophilicity and hydrophobicity originating from the temperature change. This composite hence possesses the thermoresponsive water harvesting and releasing property, allowing a 4.4 L kg_{sorb}⁻¹ water uptake at RH = 96% and a 98% water desorption

rate at 40 °C.¹⁹² Another example of MOF/polymer composite will be discussed in the next paragraph.

Sorbent-assisted AWH systems can also work together with other AWH improvement approaches. Figure 8a presents an example of sorbent-assisted AWH system combined with an

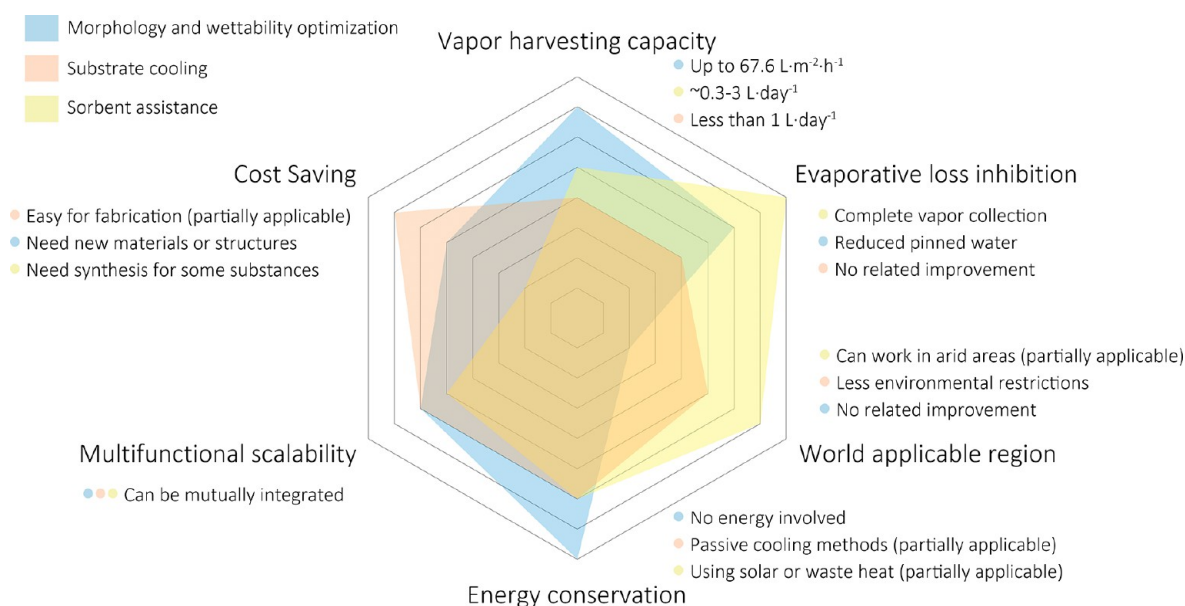


Figure 10. Performance assessment of morphology and wettability optimization, substrate cooling, and sorbent assistance strategies.

engineered surface morphology.¹⁹³ A polymer-MOF mixed-matrix is adopted, which consists of cross-linked polymer chain modified by hydroactive sites and a water-stable MOF. The proposed polymer-MOF matrix exhibits not only a great water uptake capability, but also the direct water oozing property induced by the porous configuration and reduced activation energy. Meanwhile, such material is designed to be an inverted conical array, which enables the water to be directly collected, as shown in Figure 8a. The water droplets will merge, grow, and detach from the surface, leading to an autonomous water collection merely driven by the water gravity. By virtue of the combination between engineered morphology and modified sorbent materials, a self-sustained water uptake-and-delivery system is achieved through continuous water capture and release processes. Figure 8b shows the comparison of daily water uptake between normal on–off cycle mode driven by solar energy and continuous mode without any input power.¹⁹³ It is clear that the continuous water collection rate is 4.16 L kg_{sorb}⁻¹ d⁻¹ at 90% RH, signifying a promising AWH approach with near-zero energy demand.

On the other hand, Figure 8c displays a framework of an optimized MOF system combined with a passive cooling component.¹⁹⁴ In order to promote the nocturnal vapor adsorption, the Pyromark paint is coated side up on the outside container to passively cool the inside MOF layer. The sidewalls of the container are opened at night to allow the vapor harvesting; during the day, the MOF layer will be heated in the tightly closed container by solar irradiance to release the water. Figure 8d presents the representative temperature profiles of MOF layer, condenser, environment, dew point, and solar flux versus time, with the 1.8× incidence concentration. During the adsorption cycles, an obvious decrease of temperature is observed due to the radiative cooling component, equivalent to a corresponding increase in effective RH. It enables this improved MOF system to perform a high applicability and even harvest water within arid climates.¹⁹⁴ Note that, in this case, the radiative cooling components are independent of the condensing interface, signifying that they still merely work as a detachable part of the entire system by simply embedding rather than deep integration. As a summary, Table 2 presents the

key parameters of water sorption and desorption kinetics of mentioned sorbent materials, as well as their highlighted features.

4.2. Passive Water Desorption Approaches. **4.2.1. Driven by Solar or Waste Heat.** For the sorbent-assisted AWH systems, the most commonly seen passive water desorption method is heating the sorbents by solar irradiation or waste heat. A typical example of solar-driven system is to set MOF-based water sorption unit in a day-off night-on case.¹⁹⁵ At night, the outside moisture can enter the case and can be adsorbed by the water sorption unit; during the day, the case is closed and the harvested vapor is released from the sorbents at a relatively high temperature heating by solar irradiation. Then, the vapor is condensed when contacting the relatively cool inner wall of the case and the produced liquid water can be collected from the case bottom.¹⁹⁵ Very recently, LaPotin et al. achieved a great improvement as they developed a solar-driven dual-stage AWH device, as shown in Figure 9a.¹⁹⁶ Each stage consists of an adsorbent layer and a condensing surface, separated by an air gap which enables an inner temperature gradient to be generated and maintained. The condensation latent heat on the first condensing surface can be recycled to assist the water desorption of the second stage. Consequently, the water harvesting efficiency of the proposed dual-stage system is nearly twice as high as that of the single-stage system, leading to an enhanced water harvesting capability of up to ~0.77 L/m²/day.¹⁹⁶ Note that when release is passively performed by sun heating, the maximum yield in the order of a few L/m².²¹

4.2.2. Biomimetic Alternatives. Inspired by the plant, another unique thought is that the water in hydrogels can be recovered by a moderate osmotic mechanical pressure.^{197,198} As shown in Figure 9b, the osmotic pressure exerted by plant roots in the presence of soil water, on the order of 0.1–1.2 MPa, can also be sufficient to extract water from the gel mixed with soil and so provide water to the plant roots.^{199,200} Actually, a related study that placing plant roots in the soil modified by the super moisture absorbent gels (SMAG) has been reported, as shown in Figure 9c.²⁰¹ The plant can directly take advantage of the water harvested by the SMAG soil, whose water uptake is up to 1.1 L kg_{sorb}⁻¹ at 20 °C and 90% RH, almost 2 orders of

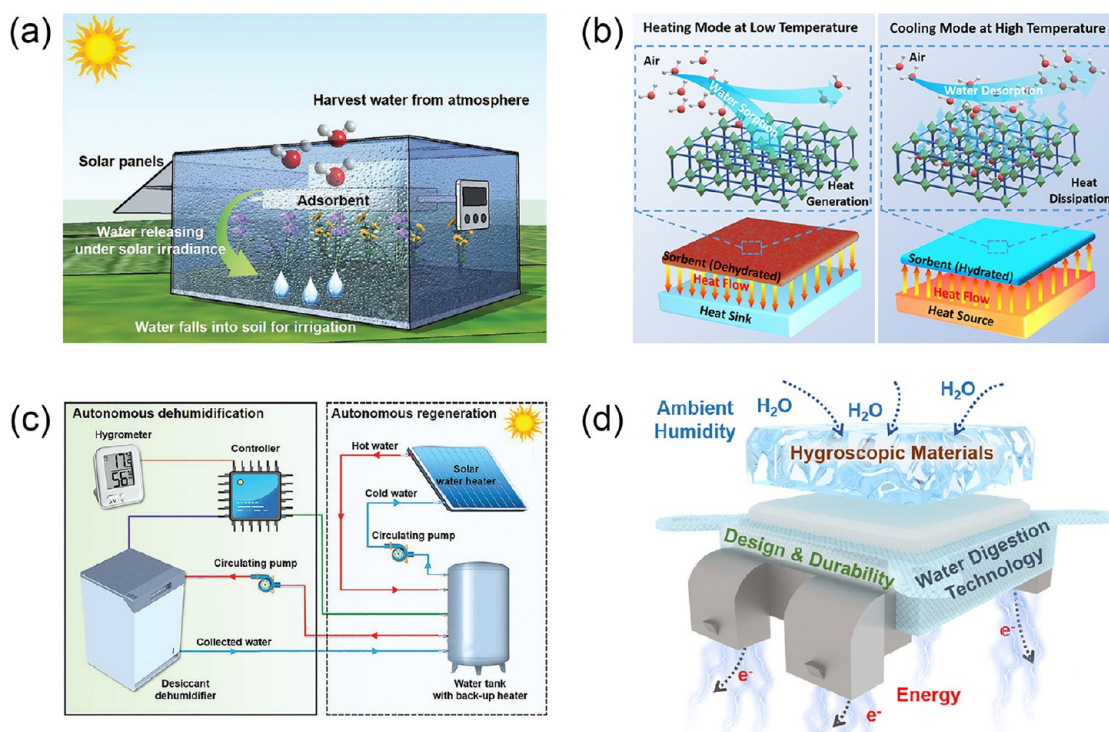


Figure 11. Applications developed based on advanced AWH technologies. (a) Schematic of a Smart-Farm system based on the Cu-complex adsorbent. [Reproduced with permission from ref 168. Copyright 2020, Wiley-VCH GmbH.] (b) Schematic of the smart thermal management based on MOF sorbents. [Reproduced with permission from ref 204. Copyright 2020 American Chemical Society.] (c) Schematic of the autonomous dehumidification/regeneration system. [Reproduced with permission from ref 169. Copyright 2021 Wiley-VCH GmbH.] (d) Schematic of the power generator based on air humidity. [Reproduced with permission from ref 206. Copyright 2020, Elsevier, Inc.]

magnitude higher than that of the sandy soil.²⁰¹ However, the main driving power of water desorption here is still solar energy, and the osmotic pressure-driven system must be further investigated. In addition, there are other natural processes that could be inspiring, such as evapotranspiration,²⁰² as well as other mechanisms of water harvesting in some plants.²⁰³

4.3. Analysis and Discussion. Compared with the water harvesting by condensation, the sorbent-assisted approaches exhibit a much wider applicable RH range and considerable water capture capacities, based on the modulation with respect to RH. The two phases of water capture and release also involve different energy and temperature demands. However, the hydrophilicity of sorbent materials inevitably makes the release of harvested water difficult, also requiring external energy supply (whatever active or passive) for the water desorption to occur through heating. Some hydrogels and composites are capable of controlling their water release temperature in the range of 40–80 °C through special design,^{167,174} but a portion of other sorbent materials hardly achieve the water release merely by passive manners. As for those materials that require a particularly low desorption energy, they usually need to work in a relative high RH.¹⁹³ There are other constraints for this class of vapor harvesting approaches. For instance, the potential sorbent leakage will corrode machinery and cause serious contamination of collected clean water. Besides, the leakage of ionic solutes will also weaken the osmotic pressure between the plant roots and the soil, which prevents plants from absorbing water properly. Thus, in future studies, the extremely strong stability and insolubility of proposed sorbent materials is mandatory, especially when used for harvesting water for human drinking and agricultural irrigation. In addition, the complicated synthesis

for some sorbents and consequent high costs should also be taken into account.

In summary, Figure 10 gives a rough performance assessment of three types of water harvesting strategies mentioned above. Apparently, each of them has their own advantages and restrictions: morphology and wettability optimization performs good improvement of water harvesting capacity of dew condensers, but is also very limited by the environmental conditions; substrate cooling may enlarge the applicable geographical regions of condensers, which however does not have significant inhibition effect on evaporative loss; for the sorbent assistance, although the wide applicable regions of some sorbent-assisted AWH systems are quite desirable, the relatively complex synthesis of substances and concomitant cost issue still cannot be ignored. Accordingly, the combination between different strategies will be one of the trends for the next generation of advanced AWH systems.

5. APPLICATIONS AND OUTLOOK

Since the humid air distributes ubiquitously and can be acquired continuously, a variety of applications derived from the AWH process have been developed in addition to water generation. In this part, we will introduce several typical AWH-based applications in different occasions. The advantages of different AWH strategies will be fully utilized in these applications. In addition, we will also present a brief outlook for the development trend of advanced AWH technologies, as well as a new concept of multifunctional AWH panel based on promising cooling materials mentioned in Section 3.1.

5.1. Applications Based on Advanced AWH Technologies. **5.1.1. Water Supply.** To provide portable water is one of

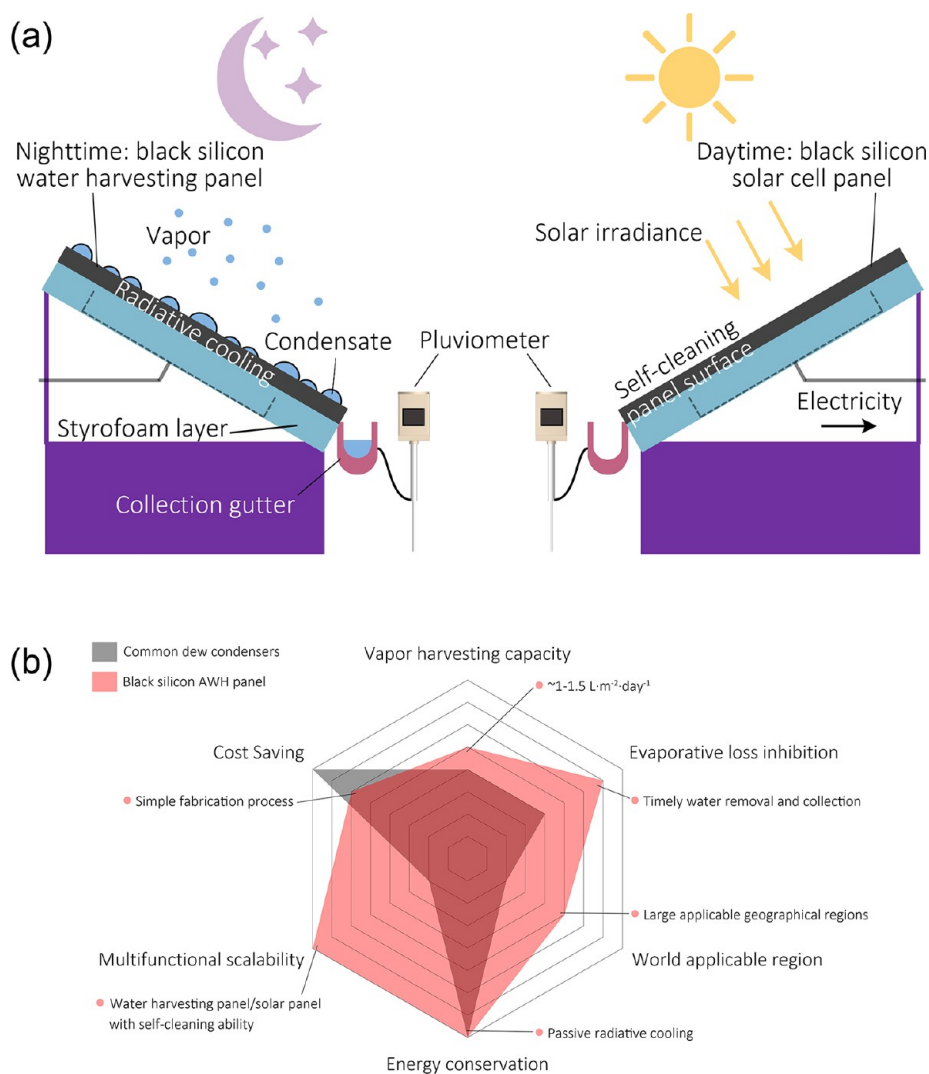


Figure 12. Concept of multifunctional water harvesting panel. (a) Schematic of the multifunctional black silicon panel. (Left) Night-time AWH system assisted by radiative cooling. (Right) Daytime solar cell with self-cleaning function. (b) Performance assessment of the black silicon panel, compared with common dew condensers.

the most common targets for AWH devices. Through surface morphology optimization, a 1 m² dew condensation panel is able to generate more than 1 L of drinkable water per night.¹¹⁹ Furthermore, each kg of MOF-801 material can generate 2.8 L water daily in an arid environment (RH ≤ 20%), which even satisfies the water demand of an adult in the desert.¹⁸⁵ Besides portable water generation, as mentioned, the AWH technologies can also be used to autonomously irrigate the plants and crops, to achieve more sustainable agriculture.^{168,201} Figure 11a presents the schematic of a Smart-Farm system on the basis of Cu-complex adsorbent.¹⁶⁸ The moisture can be captured from air and released in the chamber, and then the water flows into soil for irrigation. Based on this system, large-scale rooftop farming technology could be expanded to contribute to reducing food and water scarcity. The adsorbent can also directly work in the soil, as reported by ref 201.

5.1.2. Thermal Management. The process of water sorption–desorption involves the change of temperature and the exchange of energy. The AWH system can therefore be utilized for thermal management. For example, a smart battery thermal management approach is found based on the reversible thermal effects of MOF sorbent material, which can automati-

cally heat or cool the battery through sorption–desorption process, depending on the battery temperature.²⁰⁴ Figure 11b presents a schematic of this smart thermal management based on MOF sorbents. Such self-adaptive thermal management device can reduce the battery temperature lower than 45 °C in hot environment, while preheat the battery to 15 °C in cold environment.²⁰⁴ Similarly, a photovoltaic panel cooling strategy is also proposed by virtue of a sorption-based atmospheric water harvester, which can achieve an average cooling power of 295 W m⁻² and a temperature decrease of at least 10 °C.²⁰⁵

5.1.3. Humidity Management. By combining with machine-learning technology, the sorbent-assisted AWH device can serve as a part of the smart humidity management system with extremely low energy demand.¹⁶⁹ Cobalt-based complex is adopted as the desiccant material, being controlled by the machine-learning-assisted hygrometers to autonomously realize simultaneous dehumidification and water production. Figure 11c presents the schematic of the autonomous dehumidification/regeneration system. In a closed room, the RH can be decreased from 75% to 60% in 15 min by the proposed dehumidifier system with the energy consumption of 0.05 kWh, effectively making the living environment more comfortable.

Meanwhile, it can also harvest 10 L of freshwater in 24 h for drinking or other purposes, creating a green, low-carbon smart-home situation.¹⁶⁹

5.1.4. Power Generation. Taking advantage of humid air to generate energy is one of the recent research hotspots.^{206–209} Figure 11d shows a schematic of a typical power generator based on humidity, consisting of a hygroscopic component and a water digester.²⁰⁶ The former is responsible for continually capturing moisture from air and the latter is in charge of generating electricity by water digestion. For instance, a reported ferroelectric-semiconductor hybrid material can generate current during water oxidation, with the assistance of solar irradiance.²⁰⁷ A superhygroscopic hydrogel is combined into the digester to continually harvest moisture. This intelligent assembly can provide a photocurrent of 0.4 mA cm⁻² under an illumination of 10 mA cm⁻².²⁰⁷ Scientists also used protein nanowires to serve as the power generator.²⁰⁸ An ~0.5 V sustained voltage is generated across the 7- μ m-thick protein film with a current density of ~17 mA cm⁻², which is driven by the self-maintained moisture gradient in the film.²⁰⁸ Generally, this technology provides an option of decentralized distribution for power generation, which can minimize the related infrastructure cost. Besides, generating power from humid air can avoid carbon emissions or hazardous pollutants, offering a stable and environmentally friendly alternative for energy supply.

5.2. Outlook: New Concept of Multifunctional AWH Panel. According to Figure 10, each AWH strategy has its own advantages and limitations, the combination between different AWH methods is consequently becoming one of the popular research trends. Actually, much efforts have already been devoted to the study of multistrategies-enhanced AWH systems, as mentioned by refs 95, 96, 193, and 194. Herein, based on the promising material, black silicon, mentioned in Section 3.1, we would like to introduce an example of combination between unique surface morphology and radiative cooling ability. Inspired by the solar cell panel for harvesting energy, the scalable black silicon vapor harvesting panel can be theoretically proposed, as shown schematically in Figure 12a. The large-area of a truly superhydrophobic black silicon substrate is obliquely set on the thermal-isolated Styrofoam layer, and the condensate generation will be promoted by the radiative cooling effect of black silicon at night. Because of the slippery surface, the generated water can easily depart from the condenser surface, which is able to reduce the evaporative loss. Subsequently, the condensate is collected by a gutter at the bottom of the substrate, and the water harvesting capacity is evaluated by a pluviometer. In addition, such a proposed condenser possesses excellent scalability, because of the silicon-based substrate, for example, the solar energy harvesting function during the day. Black silicon is naturally an ideal absorber for solar irradiance, and is moreover capable of generating current by photovoltaic effect within the silicon-based substrate, which is the foundation of solar cell design. Furthermore, this optimized microstructured surface may also enable the panel to achieve the self-cleaning function¹²³ and guarantee a high solar spectrum absorptivity, promisingly leading to an efficient solar cell panel during the day. The feasibility of such multifunctional self-cleaning solar panel has been theoretically validated by Li et al.²¹⁰ On the other hand, integrating several systems including AWH devices in order to achieve one common target is currently another research trend, according to the application examples in Section 5.1. In contrast, our proposed novel concept of a black-silicon-based multifunc-

tional panel provides another thought, namely, establishing one system to realize multiple functions.

As shown in Figure 12b, the proposed black silicon AWH panel overall provides remarkable advantages, including (i) predictably considerable water harvesting capability compared with common dew collectors due to the embedded radiative cooling characteristics of the surface where condensation occurs; (ii) less evaporative loss, achieved by the microstructure-driven condensate fast removal; (iii) larger applicable geographical regions over the globe than common dew/fog condensers; (iv) less energy consumption, even fully energetically passive, compared with Peltier coolers; (v) strong scalability thanks to silicon processing facilities, signifying an easy integration of various functions; and (vi) relatively low cost, as a result of simple fabrication process of black silicon, especially for the chemical methods.^{108,109,119}

Finally, the following items should also be noted during the design of such silicon-based dew water harvesters:

- (i) Since the working temperature of condensers is lower than the ambient temperature, the atmospheric thermal radiation toward condensers is unfavorable to the radiative cooling and should be suppressed as much as possible. It requires low emissivity except in the atmospheric window waveband. Appropriate modifications (e.g., adding gratings on surfaces)²¹¹ are desirable to achieve the preferred selective absorptivity.
- (ii) To maximize the outward radiation power from the substrates, the high emissivity of the proposed panel should persist at large angles.^{64,212} Therefore, an evaluation of the angular sensitivity of black silicon is needed.
- (iii) The surface of the proposed panel must be exposed to the air in order to harvest the vapor, whose radiative cooling effect therefore will be influenced by the thermal conduction and convection with air, much weaker than those of other closed coolers.¹³⁵ Hollow forms or windshields placed around should be adopted to suppress the heat convection induced by wind.
- (iv) Besides its self-cleaning capabilities, the mechanical robustness and anti-aging abilities of black silicon must be further evaluated.

6. CONCLUSION

Generally, the AWH capability can be improved by three types of strategies: optimizing morphology and wettability of condensers; cooling the substrate; being assisted by sorbent materials. Taking appropriate measures can make the promoted AWH processes completely passive without extra energy demand. Collecting water by dew and fog harvesting is normally applicable to the moist areas, whose water nucleation, transport and collection can be accelerated by the optimized condenser surfaces; Cooling the substrates can trigger and promote dew condensation and reduce the requirements of water collection on environmental humidity. On the other hand, capturing vapor by sorbent materials has a wider applicable RH range and a better water harvesting capability, which can be used even in arid areas. According to the different advantages of these AWH strategies, they are widely applied in various occasions, either individually or as a component of integrated systems. Different AWH strategies can also be used together, which may effectively avoid their respective limitations. In particular, promising cooling materials, such as black silicon, can be considered as

the core of a new concept of scalable AWH panel, providing possibilities to realize multiple functions by one device, for instance simultaneous water and energy harvesting.

AUTHOR INFORMATION

Corresponding Authors

Daniel Beysens – *Physique et Mécanique des Milieux Hétérogènes, CNRS, ESPCI, PSL Research University, Sorbonne Université, 75005 Paris, France; OPUR, 75016 Paris, France;* orcid.org/0000-0002-7557-4928; Email: daniel.beysens@espci.fr

Tarik Bourouina – *ESYCOM Lab, UMR 9007 CNRS, Univ Gustave Eiffel, 77454 Marne-la-Vallée, France;* orcid.org/0000-0003-2342-7149; Email: tarik.bourouina@esiee.fr

Author

Xiaoyi Liu – *School of Optoelectronic Science and Engineering & Collaborative Innovation Center of Suzhou Nano Science and Technology and Key Lab of Advanced Optical Manufacturing Technologies of Jiangsu Province & Key Lab of Modern Optical Technologies of Education Ministry of China, Soochow University, Suzhou 215006, China; ESYCOM Lab, UMR 9007 CNRS, Univ Gustave Eiffel, 77454 Marne-la-Vallée, France;* orcid.org/0000-0001-7406-7732

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsmaterialslett.1c00850>

Notes

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