water

Review

Atmospheric Water Harvesting with Metal-Organic Frameworks and Their Composites: From Materials to Devices

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Abstract: Clean water scarcity is deteriorating because of the growing population and water pollution. New methods to harvest freshwater from non-traditional water sources are urgently required to address this global issue. The atmosphere contains abundant water resources. Harvesting fresh water from the air has become an emerging and attractive approach, among which sorption-based atmospheric water harvesting (AWH) is the most promising method, as it demonstrates high water producibility, wide applicability and low energy consumption. Metal-organic frameworks (MOF) are a class of emerging porous materials characterized by their large specific surface area, adjustable pore structures and chemistry. Recently, hydrolytically stable MOFs have been used as sorbents in AWH, and several MOF-based prototyping devices have been demonstrated with great practical potential. In this review, we briefly summarize the recent progress on the MOFs and their derived composites as AWH sorbents. Then, we introduce several most representative devices using MOFs for practical applications. Finally, the challenges and perspectives of this emerging field are discussed.

Keywords: atmospheric water harvesting; metal-organic frameworks; absorbent; device

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1. Introduction

Water is the source of life and a critical resource for social development. Although Earth is an enormous reservoir of water with 1.3 billion cubic kilometers in quantity, only 3% of which is freshwater [1]. However, most freshwater exists in the form of glaciers and underground water, leaving only 0.3% of the total freshwater available for direct utilization [2]. It is reported that two-thirds of the global population, i.e., around 4 billion people, live with severe water shortages [3]. The growing global population and the deteriorating water pollution put further pressure on the water shortage problem. To address water scarcity, novel materials and technologies are developed and implemented to extract freshwater from unconventional water sources, such as seawater, wastewater, and rain. However, these technologies, including seawater desalination [4–6], industrial wastewater purification [7,8], etc., are extremely energy-intensive and often require large-footprint infrastructures, thus only suitable for large cities with centralized water and electricity supply system. Unfortunately, regions where freshwater is scarce are often short of electricity supplies, and the land space is limited, such as deserts, islands, and remote rural areas [6]. Therefore, the prevailing technologies for centralized clean water supply are not suitable for these remote areas.

There is an urgent need to develop other decentralized water supply methods that can harvest fresh water from alternative water sources in an energy-saving and small-scale manner to satisfy the needs of these regions. The atmosphere contains a tremendous amount of water in the form of molecular vapor and small droplets. The total atmospheric water content is estimated to be 13,000 trillion liters, about six times as much water as rivers and lakes [9], which is enough to satisfy the drinking and agricultural needs of the world [10]. Harvesting freshwater from the atmosphere is thus a promising method to provide water for remote areas without centralized infrastructures, where both natural surface water sources and electricity are scarce.

Generally, there are three approaches for atmospheric water harvesting, i.e., fog harvesting, dew collection driven by chillers, and sorption-based AWH (SBAWH). Fog is formed by micro-sized water droplets suspended in the atmosphere. These droplets tend to grow in size, driven by their surface tension, until they are large enough to be separated and collected by gravity [11]. A fog trap net can be used to capture the small water droplets floating in the air by favoring the growth of the water droplets, after which the gathered water is available for utilization [12–14]. Fog collection from the air has been put into practice to supply fresh water. For example, inspired by the Namib Desert beetle’s shell that can collect water droplets from fog, researchers designed and fabricated devices for fog capture. These devices have been practically implemented in the coastal mountains on the edge of the Atacama Desert in northern Chile [15]. However, this method requires a local environment with near 100% relative humidity (RH) to be effective. Such stringent requirement seriously limits its practical application only to coastal and hilly areas [16]. Dew collection involves a phase change process where the vapor molecules of water transform to aqueous water when the air is cooled below its dew point, i.e., the temperature at which the water vapor is saturated. The cooling process generally consumes large amounts of energy to overcome sensible heat and latent heat of water during condensation [17,18]. Moreover, the efficiency and applicability of dew collecting depend on seasons and regions because the dew point varies with the temperature and RH of the outside environment. Such an approach is not suitable for dry and hot conditions, where the dew point can be extremely low [13].

In contrast, for the sorption-based atmospheric water harvesting approach, solid or liquid desiccants with strong hygroscopicity are used to gather the moisture from the air spontaneously and then desorb the vapor with a temperature or pressure swing [19]. The released water vapor condenses back to aqueous water in a confined space with high local humidity and is collected for usage (Figure 1). Compared to dew collection, the critical advantage of sorption-based AWH is that it greatly increases the dew point by creating a high local humidity environment in the vicinity of the sorbent. Thus, this approach is applicable even in arid regions and greatly reduces energy consumption. Solar energy and even low-grade waste heat are possible to drive the desorption of the water molecules from the desiccants. Therefore, sorption-based AWH is the most promising approach for decentralized water supply, especially in low-RH environments, and has attracted tremendous research attention [20,21].

The sorbent material is the core of the SBAWH approach. An ideal sorbent for AWH should have excellent hydrolytic stability, high water uptake capacity, fast sorption-desorption kinetics, and low regeneration temperature. So far, several porous solids and hygroscopic salts have been studied and implemented under certain practical conditions. For example, silica gels can attract water molecules with their abundant polar hydroxyl groups by the formation of hydrogen bonds, and they are widely and commercially used desiccants due to their non-toxicity, commercial availability, and facile regeneration [22]. Nevertheless, their water production performance is limited by the low sorption capacity [23]. Zeolites are another classical desiccant that shows high water uptake capacity and fast sorption kinetics due to their porous structures. They can adsorb water molecules even at extremely low RH because the open metal sites bind strongly with water molecules [24,25]. However, the strong affinity toward water molecules makes the regeneration of zeolites difficult and energy-intensive [26]. In contrast to the physical adsorption process by the silica gel and zeolites, hygroscopic salts, e.g., LiCl and $CaCl_2$, capture moisture by a rapid chemical hydration process [27]. Hygroscopic salts show the highest water uptake capacity among all common desiccants, as they can continuously absorb water until salt particles dissolve in the captured water and form liquid absorbent, which continues to absorb moisture, i.e., the deliquescence process [28,29]. However, the deliquescent characteristics of the salts will lead to the contamination of collected water by the salt ions, which could also result in the corrosion of devices. Moreover, the repeated dissolution and precipitation of the salts can result in a change in particle size and morphology, limiting their long-term cycling performance. Therefore, designing and synthesizing novel sorbent materials with the desirable water sorption and desorption characteristics is still of great significance.

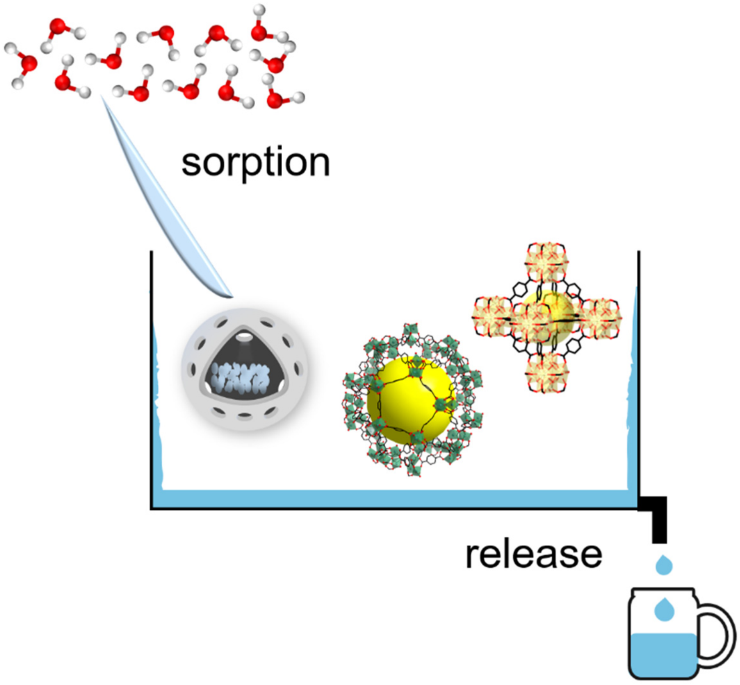

Figure 1. Schematic illustration of the working process of sorption-based atmospheric water harvesting.

Metal-organic frameworks (MOFs) are a kind of crystalline porous materials with well-defined intramolecular pores formed by the organic ligands and metal ions or clusters [30,31]. Owing to the intriguing properties of their rich and tunable pore structures and chemistry, MOFs have shown promising potential in a wide range of applications, such as gas storage, molecular separation, and catalysis [32–35]. The ultrahigh porosity of MOFs makes them ideal candidates for water adsorption, evidenced by the step-shaped isotherm profiles of many MOFs. A Step-shaped water adsorption isotherm indicates that water can be uptake and released in a relatively small temperature and pressure difference, potentially leading to an energy-efficient ad-/desorption process. Therefore, MOF is believed to be the most promising material for SBAWH and has attracted increasing research attention. Furthermore, their tunable surface chemistry made it possible to composite with various other materials to bring more synergy and multi-functionalities to SBAWH.

In this review, we will briefly introduce the materials and devices for SBAWH based on MOFs and MOF-based composites. First, we will overview water-adsorbing MOFs and discuss their performance with different water adsorption mechanisms. Then, we will introduce some MOF-based composites by highlighting their integration among individual advantages of MOFs and other functional elements. Next, devices for SBAWH will be introduced to map out their potential engineering designs toward practical applications. Finally, we will discuss the remaining challenges and future directions in terms of both material and device aspects. We hope this review could stimulate more research interest in this important and emerging research field.

2. MOFs for Sorption-Based AWH

The chemical and structural stability of MOFs in the presence of water is the fundamental request for them to be usable as AWH sorbents. Although most MOFs collapse upon exposure to water, recent research has demonstrated many hydrolytically stable MOFs by the proper choice of metals and ligands. Generally, secondary building units (SBU) with high connectivity, strong metal-ligand bonds, and hydrophobic ligands could result in MOF with high water stability. For example, M_6O_8-type (M = Zr^{4+}, Hf^{4+}) and M_3O-type (M = Al^{3+}, Fe^{3+}) SBU with pyrazole- and carboxylate-based ligands have demonstrated excellent hydrolytic stability, such as UIO-66 and MIL-101. A host of hydrothermally stable metal-organic frameworks have been studied as potential sorbents for SBAWH applications [36–41]. Table 1 provides a summary of representative MOFs and their critical parameters, including the inflection point and the saturated uptake capacity, in AWH's application.

Table 1. MOFs used for sorption-based AWH.

MOF Sorbents	Linker	BET (m^2 g^{-1})	Inflection Point (P/P_0)	Sorption Capacity (P/P_0 = 0.9)/g g^{-1}	Ref.
CAU-10-H	m-BDC	600	0.3	0.36	[39,42]
UIO-66(NH_2)	(NH_2)BDC	1123	0.2	0.38	[43]
(Ni)MOF-74	DOBDC	800	0	0.53	[44]
MOF-303	HPDC	1335	0.1	0.44	[45]
(Al)MIL-53	BDC	1040	0.1	0.09	[43]
MOF-801	Fumarate	990	0.07	0.45	[40]
UIO-66	BDC	1105	0.25	0.44	[46]
(Mg)MOF-74	DOT	1250	0	0.75	[47]
(Cr)MIL-101(NH_2)	(NH_2)BDC	1790	0.36	0.83	[43]
(Cr)MIL-101	BDC	3070	0.4	1.29	[48]
(Cr)MOF-1	TCPT	4549	0.58	1.95	[49]

The water vapor adsorption by MOFs follows three mechanisms: (1) chemisorption on open metal sites, (2) pore-filling process by water cluster formation, and (3) capillary condensation. The most typical example of chemisorption on open metal sites is studied with the (M)MOF-74 (M = Mg^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}) series. (M)MOF-74 crystals have one-dimensional hexagonal-shaped pores formed by helical chains of octahedron SUBs linked to linear DOT (2,5-dihydroxy-terephthalic acid) ligands. One oxygen in each SBU is from coordinating water, which residues toward the center of the hexagonal pore. The coordination water can be removed upon activation, leaving an unsaturated metal site, which was proved by DFT calculations on (Mg)MOF-74 (inset picture of Figure 2a) [50]. X-ray diffraction (XRD) characterizations on hydrated (Zn)MOF-74 showed the presence of three water absorption sites of various strengths, represented by three different sizes of thermal ellipsoids, which can indicate the magnitudes and directions of the thermal vibration [51,52]. In Figure 2a, the unoccupied coordination sites of the Zn atoms attract water molecules and bind them tightly by chemisorption, reflected by the smallest ellipsoids. The water molecules near the SBUs are physically absorbed, and they have larger ellipsoids, and the largest ones represent the loosely bound water molecules in the pore center. The adsorption isotherms of the MOF-74 series have the initial steep slope shown in Figure 2b, which is due to the chemisorption on metal sites of water molecules. Water molecules are absorbed tightly so that the sorbents need high thermal energy to regenerate, which is undesirable for sorption-based AWH applications.

The pore-filling process that is often adopted by microporous MOFs involves two steps. First, water molecules are adsorbed on the primary sites of the pores, usually polar and hydrophilic centers. Then, these adsorbed water molecules can act as secondary sorption sites to adsorb other water molecules into the pores to form water clusters, leading to continuous pore filling [53]. This process has been explored on MOF-303 (Al(OH)(PZDC), $PZDC^{2-}$ = 1-H-pyrazole-3,5-dicarboxylate) by single-crystal XRD characterizations and DFT calculations by Yaghi and his coworkers [45]. They explained the pore-filling sequence and mechanism of MOF-303 in detail during the water uptake and desorption process and identified the exact water adsorption sites. SCXRD analysis showed that the strongest water adsorption site of the framework was located between the pyrazoles (site I in Figure 2c), where the water molecules formed three hydrogen bonds with two N(H) atoms of the $PZDC^{2-}$ linker and one hydroxyl group of the SBU. The second and third water molecules entering the pore channel form hydrogen bonds with two N(H) atoms of the $PZDC^{2-}$ linker (site II) and the remaining hydroxyl group of the SBU (site III), respectively. Then, the subsequent water molecules fill pores by forming hydrogen bonds with water molecules residing at sites I and II, forming water clusters at site IV. They fill the pores by interacting with other water molecules rather than with the framework itself. The first water molecules are attached and bound tightly with polar centers, reflecting in the isotherm as an additional step at low vapor pressure, as shown in Figure 2d. Analogously, the formation of ordered water molecule clusters was found in a zirconium-based MOF, i.e., MOF-801, by XRD and neutron diffraction characterizations [40]. The appropriate pore size makes the zirconium SBUs of MOF-801 form hydrogen bonds with water molecules to continuously adsorb water vapor from the air. MOFs adsorbing water molecules following the pore-filling mechanism have small pore volumes and thus often have small adsorption capacities. The water sorption capacity of MOF-801 and MOF-303 is both less than 0.5 g g^{-1}.

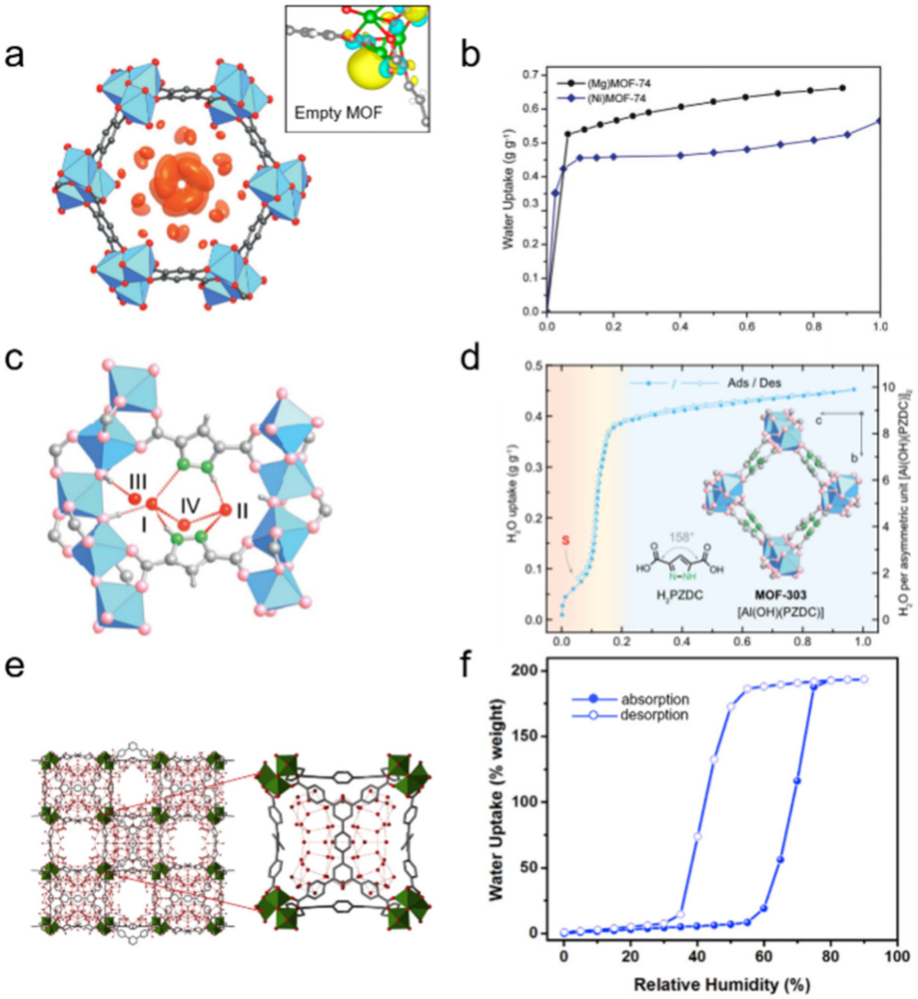

Figure 2. (**a**) Thermal ellipsoids of the different water molecules in the framework. Inset: DFT result of the open metal site. (**b**) The adsorption isotherms of MOF-74(Mg) and MOF-74(Ni). (**c**) Schematic illustration of different sorption sites of MOF-303 in the pore-filling process. (**d**) The adsorption isotherms of MOF-303. (**e**) Water molecules cluster in the cubic cages of Cr-soc-MOF-1. (**f**) The adsorption isotherms of Cr-soc-MOF-1.

The last mechanism is capillary condensation, which is mainly involved in mesoporous MOFs [52,54]. Owing to the large pore size, water molecules are adsorbed and condensed inside the porous channels. Reversing this process consumes more energy than the other two mechanisms. Using long organic ligands to increase the pore volume can improve the water adsorption capacity of MOFs. For example, Cr-soc-MOF-1 with ultra-high porosity has a record water adsorption capacity of 1.95 g g^{-1} at 70% RH (Figure 2e,f) [49]. However, the larger pore volume could lead to more energy consumption to regenerate the MOFs due to capillary condensation, reflected as the hysteresis loop in the isotherm [19,52,55].

3. MOF-Based Composites for Sorption-Based AWH

Compared to traditional desiccants, MOFs have shown advantages in sorption-based AWH in terms of low humidity performance and ideal step isotherms. However, single-component MOFs may not satisfy the practical needs as they are still limited by low water uptake capacity and energy-intensive regeneration process. Composites of MOFs with other functional materials by chemical synthesis and physical impregnation have been prepared to bring a synergistic combination of their respective merits. In this section, we will briefly discuss various types of MOF-based composites and their water sorption performance. Table 2 summarizes the characteristics of these composites.

Table 2. Summary of MOF-based composites for ABAWH.

MOF-Based Composites	Functions of Each Component	Sorption Capacity (g g^{-1})	Ref.
LiCl@MIL-101(Cr)	LiCl: absorber; MIL-101(Cr): supporting matrix.	0.8 (30% RH)	[56]
$CaCl_2$@MIL-101(Cr)	$CaCl_2$: absorber; MIL-101(Cr): supporting matrix.	0.60 (30% RH)	[57]
$CaCl_2$@UiO-66	$CaCl_2$: absorber; UIO-66: supporting matrix.	0.67 (30% RH)	[58]
PAN/MIL@LiCl-PAN/CB	PAN: forming substrate membrane with MIL-101(Cr) and CNTs; MIL-101(Cr): absorber; LiCl: absorber; CB: photothermal conversion.	3.01 (90% RH)	[59]
PNIPAM@MIL-101(Cr)	PNIPAM: supporting matrix; MIL-101(Cr): absorber.	6.39 (90% RH)	[60]
MIL-101(Cr)@PNIPAM	MIL-101(Cr): supporting matrix, absorbent; PNIPAM: promoting facile regeneration.	4.4 (96% RH)	[61]
MIL-101(Cr)@GO	MIL-101(Cr): absorber; GO: enhancing water sorption.	1.58 (70% RH)	[62]
MIL-101(Cr)/PAN/CNTs	MIL-101(Cr): absorber; PAN: forming substrate membrane with CNTs; CNTs: photothermal conversion.	1.04 (98%RH)	[63]
CuBTC/AC/GO	CuBTC: absorber; AC: enhancing the stability of composite; GO: thermal conductivity.	0.67 (90%RH)	[64]

3.1. MOF-Hydrogel Composites

Hydrogels are crosslinked networks of hydrophilic polymer chains. Due to the high flexibility of the polymer chains, hydrogels tend to swell and expand upon taking up water. Therefore, they exhibit high water storage capacity. Moreover, the wide diversity of polymer types could bring the hydrogels various additional functions. Recently, the thermal stimuli-responsive hydrogel with lower critical solution temperature (LCST) has been extensively studied. The thermo-responsive polymeric hydrogel could change its wettability by its phase change according to environmental temperature. When the outside temperature is lower than its LCST, the hydrogel is hydrophilic, and it can serve as a water reservoir at the molecular level. Once the environmental temperature is higher than its LCST, the hydrogel becomes hydrophobic, and the adsorbed water within the hydrogel will be repelled. The unique property of this kind of hydrogel is ideal for sorption-based AWH sorbents because it can ensure easy regeneration. Several MOF-hydrogel composites sorbent by combining MOFs with the thermos-responsive hydrogel, poly (N-isopropyl acrylamide) (PNIPAM) hydrogel has been reported [60,61,65]. Specifically, Karmakar et al. prepared a thermos-responsive MOF-hydrogel composite by in-situ polymerized PNIPAM hydrogel within the mesopores of MIL-101(Cr) for water capture and heat transfer applications (Figure 3a) [61]. Pure MIL-101(Cr) has a high airborne water harvesting capacity of 1.01 g g^{-1} at 90% RH, and it functions as the major vapor adsorbing component. After loading MIL-101(Cr) with PNIPAM, the composite can largely retain the water uptake capacity of MOFs (Figure 3b). The complete desorption and release of water from pure MIL-101(Cr) requires a high temperature of around 90 °C [66]. In sharp contrast, the MIL-101(Cr)-PNIPAM composite sorbent can release nearly all of the captured water at an unprecedentedly mild condition of around 40 °C, i.e., LCST of the confined PNIPAM, due to the hydrophilic to hydrophobic transition of PNIPAM (Figure 3c). Therefore, the desorption process of the composite is much faster and requires less energy.

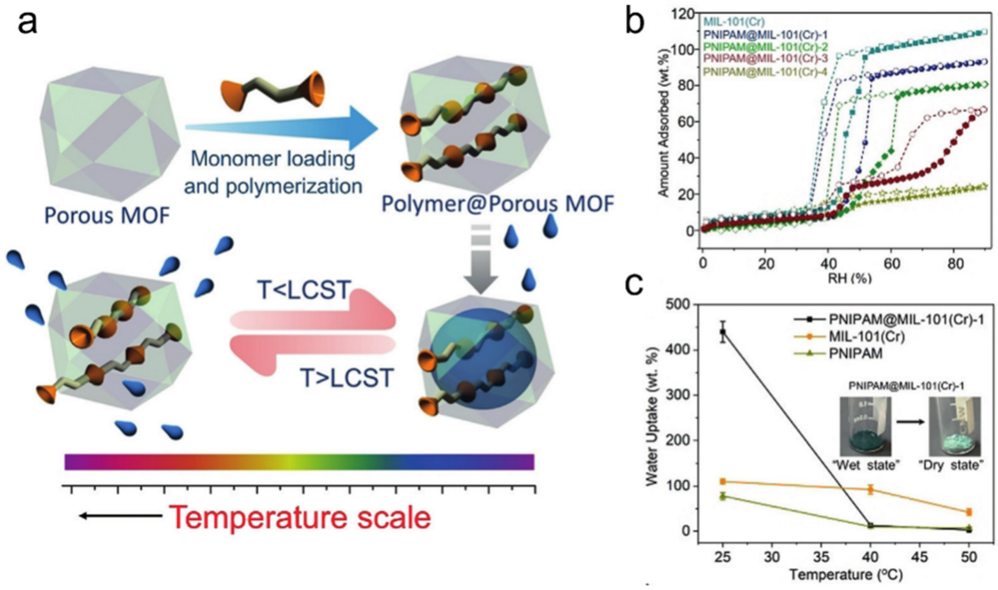

Figure 3. (**a**) Schematic illustration of the polymer-in-MOF composites and the temperature-triggered water capture and release process. (**b**) Comparison of adsorption isotherm curves of composites loaded with different amounts of PNIPAM. (**c**) Comparison of water uptake capacity in different environments.

3.2. MOF Complexed with Carbon-Based Materials

Due to the excellent photothermal property and thermal conductivity, carbon-based materials, such as CNTs [63,67], graphene oxide [64], carbon fiber [68], and carbon black [59], are also used to composite with MOFs, so the desorption process could be driven by natural sunlight or low-grade waste heat. For example, Li. et al. synthesized a novel nanofibrous membrane-loaded MIL-101(Cr) composite sorbent [63]. The nanofibers made of polyacrylonitrile (PAN) and CNTs were prepared by a free surface electrospinning process to form a nanofibrous membrane substrate, and MIL-101(Cr) was subsequently loaded onto the membrane by the spray coating method. The nanofibers are intertwined to form a multi-layer structure with open microchannels on which the MIL-101(Cr) particles are uniformly dispersed. The MIL-101(Cr) particles are mainly responsible for moisture adsorption, while the CNTs promote rapid and complete vapor desorption upon exposure to sunlight due to their high solar light absorbance and outstanding photothermal conversion efficiency. In addition, the nanofibrous substrate fabricated by the electrospinning technique provides interconnected paths benefiting the rapid diffusion of water molecules. This composite membrane shows fast ad-/desorption kinetics compared to pure MOF sorbents, and it can desorb completely only using sunlight.

Generally, an electric heater is necessary to help desorption and release water when the natural sunlight is not sufficient or the sorbent materials suffer from low photothermal conversion capability. Carbon fiber with a high electro-thermal conversion efficiency can be used as heaters to facilitate the fast desorption of a MOF adsorbent. For example, Li et al. prepared a MOF-based composite by embedding carbon fiber bundles at the center of cylindrical Al-Fumarate adsorbent loaded within sodium alginate [68]. The inner carbon fiber is coaxially connected with the outer adsorbents, which convert electricity to thermal energy to assist the desorption of Al-Fumarate. Furthermore, graphene oxide (GO) can help to improve energy efficiency by prolonging the thermal conductivity of an electrical heater for desorption. So, loading MOF and graphene oxide are expected to promote the desorption of MOFs. Laha et al. synthesized ternary MOF-clay-graphene oxide nanocomposite, including aminopropyl clay, graphene oxide, and CuBTC ($Cu_3(BTC)_2(H_2O)_3$, BTC = benzene-1,3,5-tricarboxylate) through an in situ hydrothermally synthesis process for indoor sorption-based AWH [64]. The CuBTC nanoparticles uniformly grow on the non-porous two-layered templates made of aminopropyl clay and graphene oxide. Among all the components, CuBTC mainly acts as a sorbent and graphene oxide is added because of its extended heat conductivity, which will promote water release during desorption. Although CuBTC sorbent is suitable for a wide range of RH, its instability under humid conditions limits practical use. The dynamic water-dispersible characteristics of aminopropyl clay can improve the hydrolytic stability of the ternary MOF-based composite. This composite shows a water sorption capacity enhanced by 39% compared to pure CuBTC and it can achieve facile regeneration.

3.3. Salt-in-MOF Composite Sorbents

Apart from functioning as merely a desiccant, MOF could also play an important role in composite absorbents as a matrix due to their stable porous structure. As mentioned above, hygroscopic salts have a high water-sorption capacity among all conventional desiccants. However, the deliquescence of the hygroscopic salt into liquid will cause the agglomeration of salt particles during dehydration, reducing the ad-/desorption kinetics by slowing the further penetration of subsequent water molecules and eventually decreasing the overall performance. Incorporating these salts into a porous MOF matrix has been proposed to overcome this issue [69–71]. The matrix can provide a confined and rigid space for the deliquescence and liquefaction of the hygroscopic salt. The liquefied salt was confined within the pores of MOFs due to capillary force, which prevents the hygroscopic salt from leakage and agglomeration. Consequently, this design of structure can accelerate the ad-/desorption as the diffusion of water molecules becomes less hindered. Because of their permanent porosity, large pore volume, and large specific surface areas, MOFs are an optimal choice as a porous matrix to host salts [56–58,72], referred to as salt-in-MOF sorbents.

$CaCl_2$-in-UIO-66 is one of the earliest salt-in-MOF composites to achieve adsorption-based heat transformation [58]. The spherical hollow structure of UIO-66 encapsulated $CaCl_2$ was prepared by the spray-dry method. The robust structure of UIO-66 provides spaces for the ad-/desorption of $CaCl_2$. The homogeneous distribution of Ca and Cl elements in the inter-particle voids of $CaCl_2$-in-UIO-66 superstructures shows that salts can be confined in both the inherent microporosity of MOFs and the voids between MOFs (Figure 4a). These confined salts play a crucial role in increasing the water sorption capacity of composite material. This composite sorbent shows a sorption capacity of 0.67 $g\ g^{-1}$ under 30% RH at 30 °C, which is a significant increase compared to the water absorption capacity of 0.25 $g\ g^{-1}$ for pure UIO-66 at the same condition (Figure 4b). Recently, LiCl-in-MIL-101(Cr) has been reported to incorporate LiCl in the water-stable MIL-101(Cr) by physical impregnation (Figure 4c) [56]. The large porosity and stable pore structure of the MIL-101(Cr) matrix ensure the sorption processes of salt occurs inside of the matrix without leakage and agglomeration, thus preventing a decrease in the ad-/desorption kinetics of LiCl salts. Both LiCl and MIL-101(Cr) can act as sorbents in the composite for their high water-sorption capacity. As shown in Figure 4d, this composite exhibited greatly improved adsorption kinetics compared to pure LiCl salts with a water-sorption capacity of up to 0.77 g g^{-1} at 30% RH, 30 °C. This is the highest value among salt-in-MOF absorbents for sorption-based AWH. This work shows that using hygroscopic salts as absorbents encapsulated in porous MOFs contributes a lot to the sorption capacity of sorption-based AWH materials, which will help to solve water scarcity in arid regions.

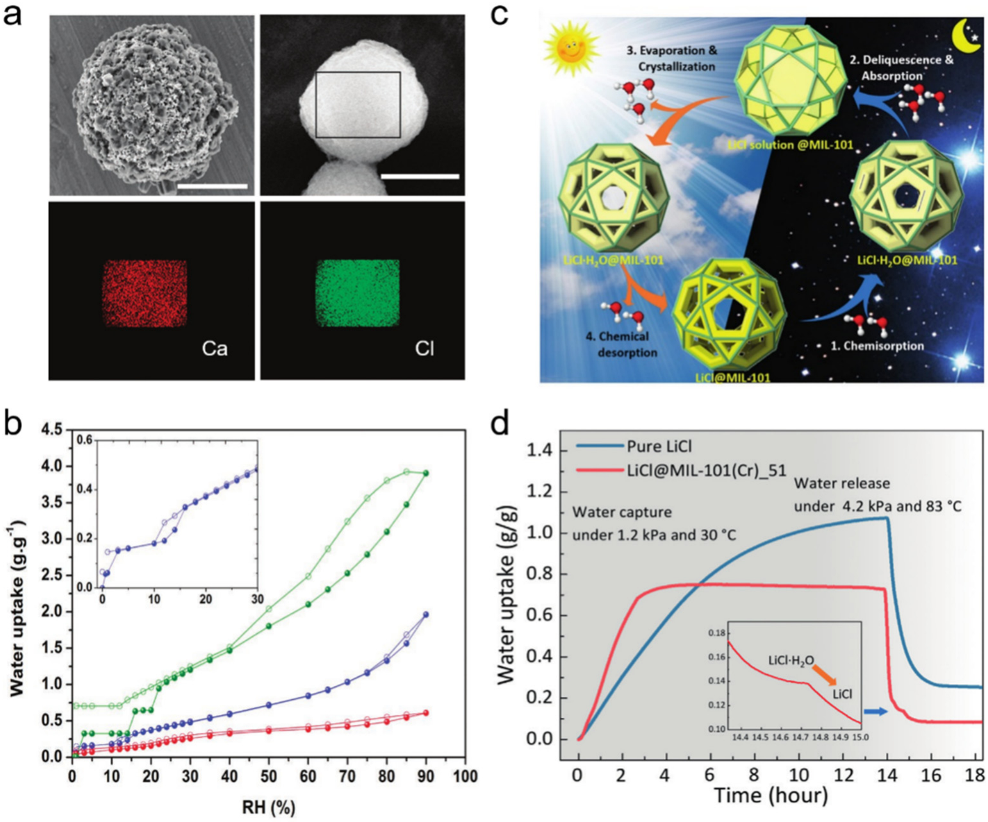

Figure 4. (**a**) SEM image and elemental mapping of $CaCl_2$-in-UIO-66. (**b**) Adsorption isotherms of $CaCl_2$ (green), $CaCl_2$-in-UIO-66 (blue) and UIO-66 (red). (**c**) Schematic illustration of a LiCl-in-MIL-101(Cr) and its AHW process. (**d**) Adsorption isotherm of LiCl-in-MIL-101(Cr).

4. MOF-Based Devices for Sorption-Based AWH

Besides the great efforts made to explore new MOFs with high water uptake capacity, fast adsorption kinetics, and low desorption temperature, the other equally important aspect of promoting the practical application of AWH is the design and engineering of energy-efficient water-harvesting devices and equipment. So far, several types of device prototypes have been reported based on different engineering considerations, which all showed promising results. In this section, we will briefly introduce the representative devices. Table 3 summarizes the characteristics of these devices.

Table 3. Summary of MOF-based devices for ABAWH.

Device Type	Configuration	Sorbents	Water Productivity (L kg_{MOF}^{-1} day^{-1})	Characteristics	Ref.
passive	Adsorption and condenser chamber, test apparatus.	MOF-801	0.25 (20% RH)	1. one adsorption half-cycle at night and one desorption half-cycle during the daytime; 2. desorb directly only using solar energy; 3. used air as the heat sink.	[73]
	The sorption unit, condenser case.	MOF-801/nonporous graphite	0.1 (5–40% RH)		[9]
active	MOF exchanger, compressor-based condenser, solar cell.	MOF-303	0.7 (10–30% RH) 1.3 (40–60% RH)	1. multiple ad-/desorption cycles a day; 2. photovoltaic power generation; 3. blows the air with fans	[37]
	MOF layer, solar simulator, acrylic enclosure, and condenser.	MOF-801	2.8 (20% RH)	1. multiple ad-/desorption cycles a day; 2. solar simulator helps to desorb 3. 3. monitor and keep the ambient temperature constant with thermocouples	[74]
adaptive	Air intake compartment, sorption compartment, condensation compartment	MOF-801	1.8 (10–30% RH) 3.52 (40–60% RH)	1. multiple ad-/desorption cycles a day; 2. monitor the environment in real time; 3. respond to the real-time data to save energy	[75]

4.1. Passive Water Harvesting Device

The major energy-consuming processes during an AWH adsorption-desorption cycle are heat-induced desorption and the cooling-induced condensation of the released water vapor. Therefore, to achieve minimum external electricity consumption, naturally abundant sunlight is the ideal energy source to power the heating, and ambient air is used as the heat sink for cooling. As a proof-of-concept, a box-in-box design was demonstrated with MOF-801 powder as the water sorbents [73]. The device consisted of a smaller inner box containing MOF-801 as the water sorption unit and a larger case outside for vapor condensation and enclosure (Figure 5a). The inner sorption unit box is made with acrylic and consists of a sorbent container, supporting walls and the thermal insulation compartment. Due to the low intrinsic thermal conductivity and light absorbance, MOF-801 was co-blended with 33 wt% of non-porous graphite powder, and around 1.65 kg of MOF/graphite was placed inside the container. MOF-801 required a desorption temperature inside the container of around 65 °C, while the condensation of water vapor at the wall of the outbox is at around 20 °C. To keep such a high-temperature difference within the device, thermally insulating polystyrene foam was attached around the walls, and all exposed wall surface was coated with high infrared reflectivity materials to minimize the thermal conduction and radiation toward the outer space of the container. The condensation of the vapor occurs on the inner surface of the outer enclosure case, which can constantly transfer the condensation heat toward the outside environment. Furthermore, an IR reflector was placed on the top of the case to ensure sunlight only reaches the saturated MOF layer but not heats the entire device. The system operates one full adsorption-desorption cycle per day, consisting of one adsorption half-cycle at night and one desorption half-cycle during the daytime. At night, when the relative humidity of outside air is high, the lid is opened, the humid air diffuses into the sorbent bed, and the sorption process starts. During the daytime, the lid is closed, and natural sunlight powers the heating of the sorbent bed by the solar-thermal effect. The released water vapor is subsequently condensed into droplets on the inner wall of the box and collected at the bottom. The integrated system can yield a maximum of 0.58 L kg^{-1} day^{-1} under the condition of 30% RH.

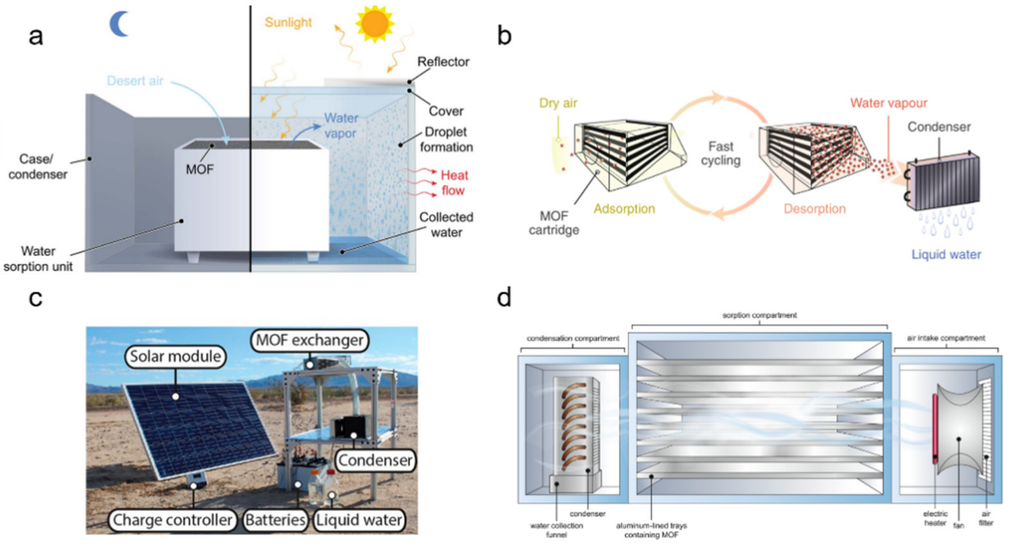

Figure 5. (**a**) Schematic illustrations of the integrated system of the passive device. (**b**) the active device. (**c**) the photo of the device prototype operating in active mode. (**d**) schematic illustrations of the adaptive device.

Operating one cycle per day, the water productivity of the passive device mainly depends on the maximum sorption capacity of the material. Due to the limited thermal conductivity and solar light absorbance, MOF-801 powder was co-blended with non-porous graphite into the sorbent bed, which could result in reduced mass-based water productivity. To enable passive cooling, it is required that the environment temperature is lower than the dew point of water vapor within the confined case. For an environment with surrounding temperatures higher than the dew point, an electric cooling apparatus can be used to condense the water vapor at the cost of higher energy consumption [9].

4.2. Active Water Harvesting Device

Devices operating on the passive mode have a stringent requirement on the sunlight and temperature of the environment, and the water productivity is limited by the maximum water uptake capacity of the MOF materials. However, it is not facile to develop new MOFs with extremely high water-uptake capacity, which are simultaneously easily produced in large quantities. Moreover, under practical conditions, the powdery sorbent material can hardly achieve its saturated vapor adsorption capacity, nor can it desorb water molecules completely because of the mass transfer resistance caused by the dense packing of the material and structural hindrance from the hardware.

From the operation perspective, a device that can perform multiple adsorption-desorption cycles could fundamentally circumvent the material limitation. Engineering devices that are capable of continuous operation and multiple ad-/desorption per day have been reported, in which the adsorption and desorption processes are electrically powered with fans, heaters, and condensers [37,71]. As a typical example, Hanikel et al. designed a sorption unit that can operate in an active mode (Figure 5b). The unit is comprised of sorbent beds, electric fans and heating strips, referred to as MOF exchangers. Powder-form MOF-303 are spread evenly between two layers of laminated microporous PTFE membrane and subsequently assembled into the exchanger with thermally conductive acrylic in an orthogonal configuration. The orthogonal configuration of the exchanger makes the sorption and desorption on the sorbent beds thoroughly by convection. Compared to passive mode devices, the mass transfer of the water molecules in the active systems has improved greatly. MOF-303 was chosen on account of its rapid kinetics to reach full saturation and complete desorption within a few minutes. During the adsorption, humid air was forced into the cartridge containing MOF sorbents by fans to saturate the MOF. To desorb the water, the heating strips are powered on to drive the release of water vapor from sorbent beds actively. The AWH system is constructed by connecting the MOF exchanger to a solar panel-charged battery system, a condenser, and water-collecting bottles (Figure 5c). The system can realize multiple operation cycles a day, compared to a single cycle of the passive mode device, for higher water production. With the solar module and batteries, this kind of device can perform the adsorption and desorption cycles even at night. This system could generate 1.3 L $kg_{MOF}{}^{-1}$ day^{-1} at 32% RH, more than twice the water generation value of passive devices under the same condition. In contrast to previous devices that mainly focused on the saturated sorption capacity of materials, this study demonstrated that controlling and exploiting the dynamic water capacity is an equally important aspect of high-efficiency water production.

4.3. Adaptive Water Harvesting Device

The active device requires some amount of external electricity input. Although natural sunlight could be used to drive the device's operation, it is still desirable to further optimize the energy efficiency of the harvester in order to promote its wider applications. A new study on the improvement of freshwater production based on multiple water harvesting cycles by engineering an innovative device was reported recently, called an adaptive water harvester [75]. The design of the sorbent system is similar to the active device described above (Figure 5d), consisting of an air intake compartment, sorption compartment, and condensation compartment. Aluminum linings were used in the sorption bed packed with MOF-801 to facilitate better heat transfer. The real-time temperature and RH of the ambient environment and each part of the adaptive device is monitored by sensors. The adaptive water harvester was programmed to read the dew point from its database according to the combination of real-time temperature and RH values, and then the algorithm instructed the ad-/desorption behavior of the device in response to the dew point values. Two algorithms are developed to calculate appropriate ad-/desorption time for the adaptive device, thus optimizing the energy efficiency. The database abovementioned is set up by collecting environmental data from the active device at the condition of 7% RH to 70% RH and calculating the corresponding dew point values using the equation. Due to the real-time responsive operation of the device, this integrated system can optimize the energy efficiency of each cycle, dramatically lowering the energy consumption of sorption-based AWH technology. The adaptive device can yield 1.8 L H_2O $kg_{MOF}{}^{-1}$ per day in the arid climate (10–30% RH) with a maximal energy consumption of 9.45 kWh, while the same device running active mode requires a 12.6 kWh power input to produce the same amount of water.

5. Conclusions and Perspective

Independent of local geographical and climatic conditions, sorption-based atmospheric water harvesting is an innovative way to achieve a decentralized freshwater supply in water-stressed regions. MOFs stand out as promising materials for their permanent porosity, adjustable chemical properties, and stable structure. MOF-based composites could simultaneously achieve improved water uptake capacity and facile regeneration, as well as realize multifunctionality through the synergy between MOF and other components. This review discusses MOFs and MOF-based composites as promising sorbent materials for moisture extraction and release, outlining the key mechanisms of vapor adsorption by MOFs with different structural types and pore sizes. Besides, the engineering considerations and operational strategies of the MOF-based water harvesting devices are discussed with passive, active and adaptive design principles.

The utilization of MOF-based sorbents in a water harvester is promising to solve water scarcity in arid regions powered by natural sunlight or other low-grade thermal resources. Significant progress has been made in both the fundamental science and practical utilization of this emerging research area of MOF-based AWH technology. However, unexplored questions and challenges remain. From the material perspective, although the pore volume and pore structure of MOFs can be tuned by adjusting metal clusters or organic ligands, their water adsorption ability, however, is still hard to predict based on reticular chemistry. More research on the water adsorption mechanisms that correlate the structure and adsorption behavior is highly needed to guide the future design and synthesis of new MOFs with higher uptake capacity and faster adsorption/desorption kinetics. In addition, large-scale production of MOFs with stable performance is still a big challenge today, which calls for more engineering exploration of a possible route for mass production. For MOF-based composite sorbents, although only a few works have been reported, they have already demonstrated great potential to improve the overall water harvesting performance. From the fundamental level, it is needed to probe how the structure of water molecules changes when diffusing in the composite absorbent during the ad-/desorption process with advanced characterization tools and simulations.

From the device perspective, the mass transfer resistance, energy efficiency, and the cost of devices are all required to be carefully evaluated when applying this technology to practice. The form of adsorbents (e.g., powder, film, bulk) and shape/structure of the sorbent unit could have a great impact on the overall mass transfer resistance of devices. However, the study merely based on isotherms of the sorbent materials does not provide direct answers. To optimize the overall energy efficiency, there is still a lot to explore regarding the choice of device material, space arrangement of each component, and operation modes. In addition, evaluation protocols and standards are needed in order to access the energy consumption of different devices more fairly. These unsolved questions require engineers and chemists to work together. The one final core target and also the greatest challenge is to transfer experimental design out of the laboratory and apply it to a productive life. We hope this review could stimulate more research effort from both chemists and engineers to further optimize current harvesting systems and look for new MOF-based sorbents.

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