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수분 수착 MOF를 이용한 건조한 지역의 대기 중 워터하베스팅 기술의 최근 동향

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Recent Advances on MOF-assisted Atmospheric Water Harvesting at Dry Regions

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요 약: 전 세계적인 물 부족을 해결하기 위한 유망한 방법으로 수착제를 이용하여 공기 중에서 물을 수확하는 기술은 수자원이 부족한 지역에서 식수를 전달할 수 있는 큰 잠재력을 보여주고 있음. 본 총설에서는 대기 중 물을 수확하기 위한 수착제로 금속유기골격구조(MOF)를 사용하는 최근 연구에 대해 소개함. 제올라이트나 실리카 기반 물질과 같은 다른 수착제 물질에 비해, MOF는 상대습도 10% 부근에서 물 수착 곡선의 변곡점을 보이는 특성 덕분에 건조한 사막지역에서 물을 수확하기에 적합한 특성을 가지고 있음. 이러한 특성으로 말미암아 최근 MOF를 이용하여 물을 수확할 수 있는 실용적인 물 수확 장치를 개발하기 위한 연구가 활발히 진행되고 있음. 이 기술은 전 세계 어느 곳에서나 지리 환경적 영향을 받지 않고 대기 중의 물에 접근할 수 있기 때문에, 미래 지속가능한 수자원 확보 기술 측면에서 새로운 패러다임을 제시할 것으로 기대됨.

Abstract: As a promising method to address global water scarcity, sorbent-assisted water harvesting from air has shown great potential to deliver drinking water for inlands lacking traditional water sources. In this article, the recent studies of using metal-organic frameworks (MOFs) as sorbents to harvest atmospheric water will be introduced. Compared to the other sorbent materials such as zeolites or silica-based materials, MOFs have shown prospective properties such as the water isotherm inflection points as low as ~10%, which are suitable for harvesting water at dry regions. Due to this property, recently, MOFs have been extensively adopted to develop practical water harvesting devices that can harvest water. Since atmospheric water is accessible anywhere and anytime in the world, this technology is expected to open a new avenue in terms of securing safe water for the future.

Keywords: *atmospheric water harvesting, metal-organic frameworks, covalent-organic frameworks, water scarcity*

1. Introduction

Water is essential to life. However, more than two-thirds of the global population suffers from water scarcity, making it one of the world's greatest challenges[1]. Additionally, recent environmental issues such as carbon emissions have exacerbated temporal and regional imbalances in accessible fresh water worldwide. As a result, the availability of traditional water sources, such as surface and groundwater, has diminished over the past few decades[2,3]. The demand for alternative water sources, in preparation for the future water crisis, has exponentially increased. In this perspective, one of the most successful and repre-

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sentative alternative water sources is seawater. In the past, seawater was not considered a viable source due to high energy costs and environmental concerns related to desalination processes. However, recent developments in seawater desalination technologies, especially reverse osmosis (RO) desalination using semi-permeable membranes, have made seawater a sustainable water source[4].

Even though seawater desalination has shown remarkable success, this technology cannot be a universal solution to address the global water crisis[5]. This is because not every region in the world is close to the shoreline and has enough access to seawater, posing a significant limitation. This challenge is particularly acute for countries that experience severe water stress, such as those in Africa. Therefore, the development of sustainable technologies to secure fresh water everywhere is of urgent importance.

The sorbent-assisted atmospheric water harvesting (AWH) has emerged as a promising technology to help resolve such challenges, especially in areas suffering from year-round water shortages (Fig. 1)[6,7]. This innovative approach involves using microporous materials to extract water from the air and release it into small containers, producing drinkable liquid water. The process relies solely on natural sunlight and ambient temperatures, leaving no environmental footprint. Since water in the air is ubiquitous on earth, it holds the potential to provide fresh water anywhere in the world. However, for this technology to make a global impact, more systematic studies are needed, focusing on both (1) the development of new porous materials (sorbents) and (2) the design of sorbent-integrated devices, referred to as water harvesters. These studies are crucial to enable practical water harvesting for human consumption, particularly in dry regions. In this article, the recent progress of MOF-based atmospheric water harvesting technology will be overviewed, concluding with perspectives on the future directions of this innovative approach.

2. AWH

Harvesting water from the air is not a new concept, as it has long been recognized that water exists in the atmosphere as vapor worldwide. Consequently, various attempts have been made to extract atmospheric water for daily use. For instance, in regions where fog is a common occurrence, like California, hydrophobic nets are strategically placed in the path of air advection. Colloidal water droplets adhere to the surface of these hydrophobic nets, coalesce, and are then removed by gravity, collecting in a harvesting barrel (Fig. 2)[8,9]. This technology, known as fog-catching, has demonstrated success in providing practical amounts of water for human activities. However, its applicability is limited to regions where fog is frequent. It is worth noting that such regions may not experience severe water

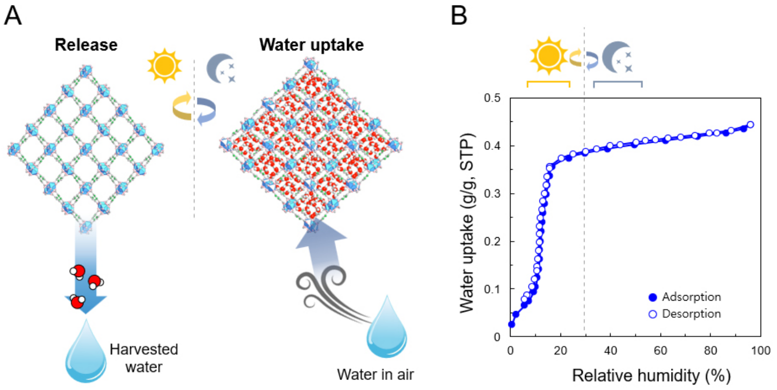

Fig. 1. Schematic illustration of AWH mechanism using MOFs as sorbents during the day-and-night cycle. Reproduced from the ref [7]. Copyright© Springer Nature 2022.

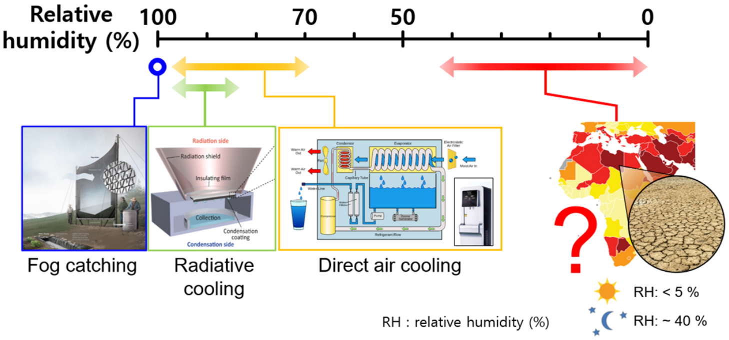

Fig. 2. Conventional AWH techniques and their corresponding RH conditions that are energetically viable. Radiative cooling figure is reproduced from the ref [10]. Licensed under the CC BY-NC.

stress, as humidity levels need to be sufficiently high for dewing to occur.

Another example is radiative cooling (Fig. 2)[10-12]. Any object with a temperature emits energy to its surroundings in the form of radiation. If this energy emission is more efficient than the receiving energy from the surroundings through heat convection, the body's temperature can be maintained lower than the ambient temperature. This phenomenon is known as radiative subcooling. Recently, Haechler *et al.* developed a radiative cooling system by designing a radiation emitter that facilitates energy emission to the universe under clear sky[10]. They demonstrated that this system can maintain a temperature up to ~15°C lower than the ambient temperature, allowing the air to reach dew conditions. Consequently, they could harvest water from the air without any external power, even in regions where humidity is lower than 90%.

The last representative AWH technology is direct air cooling (Fig. 2)[13]. The mechanism of this AWH resembles that of air conditioners, which use adiabatic expansion of fluids to cool the air and, consequently, harvest water as the air quickly reaches dew points due to abrupt temperature changes. However, this technique is energy-intensive and only cost-effective when the relative humidity (RH) of the air is higher than 70%. Therefore, while the above three AWH categories have demonstrated the ability to harvest atmospheric water, they may not be practical, especially in regions where sustainable water sources are urgently needed.

3. AWH Using MOFs

In 2014, Yaghi and his colleagues recognized that a series of zirconium(IV)-based MOFs, including MOF-801, could capture water from the air at room temperature, exhibiting water isotherm inflection points at around ~20% RH.[14].Moreover, MOF-801 demonstrated a water capture capacity of ~42 wt%, and the sorbed water could be desorbed from the MOFs without hysteresis upon gentle heating at 45°C. The combination of high-water uptake capacity, the ability to be regenerated by mild heating, and water sorption starting at RH as low as ~20% promptly sparked the idea of using MOFs to harvest water from the air, even in arid climate conditions. Motivated by this concept, Yaghi from UC Berkeley and Wang from MIT collaborated in 2017 to demonstrate that MOF sorbents could harvest atmospheric water into a liquid form using sunlight as a major energy source[15]. Following this groundbreaking work, numerous studies have been published exploring the potential of MOFs and other functional sorbent materials for sorbent-assisted atmospheric water harvesting as a sustainable technology.

4. MOF Properties for Atmospheric Water Harvesting in Arid Regions

For the successful implementation of MOF-based Atmospheric Water Harvesting (AWH) in dry regions, the following MOF property criteria have been pro-

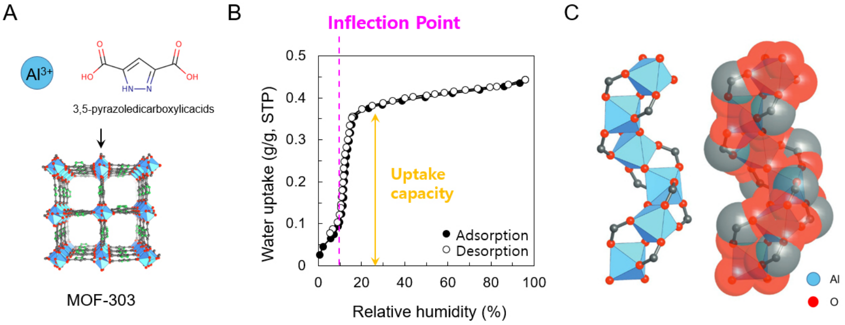

Fig. 3. MOF-303. (A) Building blocks of MOF-303; aluminum ion and 3,5-pyrazoledicarboxylate. (B) MOF-303 water isotherm at 25°C. (C) Sterically shielded 1D SBU structure of MOF-303 that result in good hydrolytic stability. Panel (C) is reproduced from the ref [19]. Copyright© 2018 John Wiley & Sons, Inc.

posed (Fig. 3)[6,16,17]: (1) high water uptake capacity, (2) an inflection point of the water isotherm as low as ~10% RH, (3) low heat of water sorption for efficient sorbent regeneration (water desorption and harvesting), and (4) hydrolytic stability. While numerous MOF materials have been proposed to meet these criteria, one of the most widely adopted MOFs is the aluminum-based MOF-303[18]. These MOFs are synthesized using Al^{3+} and 3,5-pyrazoledicarboxylate as building blocks (Fig. 3A). MOF-303 has become a hallmark for AWH applications due to its exceptional hydrolytic stability, a challenge faced by many other MOFs due to inherent material properties. For instance, many MOF materials are not stable upon exposure to water, as partially charged oxygen molecules can exchange organic linker-metal ion coordination bonds, leading to structural breakdown. However, in the case of aluminum-based MOFs, including MOF-303, aluminum metal centers are aligned to form 1D secondary building units (SBUs), and these metal centers are sterically shielded by alternatively rotating carboxylate groups, preventing physical access of water molecules to the metal centers and linker exchange (Fig. 3C)[19].

Furthermore, breaking new ground in the field, Hanikel *et al.* conducted a groundbreaking study using single crystal X-ray diffraction (SCXRD) to reveal how water molecules evolve within the micropores of MOFs during the water sorption processes as relative humidity (RH) gradually increases[20]. This investigation demonstrated that only a limited number of water molecules are directly sorbed at the backbone of MOFs, while the remaining water molecules evolve and fill the pores, forming water clusters in nano-confined environments. These distinctive pore-filling mechanisms contribute to the low heat of sorption, approximately ~48 kJ/mol, comparable to the heat of evaporation of water (~44 kJ/mol), showcasing the energy-efficient nature of water desorption. Presently, utilizing MOF-303 as a foundational structure, a variable version of organic linkers with dicarboxylates has been introduced to develop new MOF materials with increased water harvesting capacity. This approach aims to maintain MOF-303's exceptional hydrolytic stability and energy efficiency for water desorption.

5. Atmospheric Water Harvester: AWH devices with scalable amount of MOFs

In the pursuit of AWH research to provide sustainable water to global communities, it is crucial to develop scalable water harvesting devices that incorporate MOFs as sorbents. In 2017, Fathieh *et al.* introduced a straightforward box-in-box water harvesting device design, termed a water harvester (Fig. 4)[18]. The researchers tested this device using 1.2 kg of MOF-801 as sorbents in the Arizona deserts during October. In essence, this device featured a tray where MOF-801 powders were distributed, exposed to the air during the night when the relative humidity (RH) increased to ~40%, even in the desert. During these night cycles,

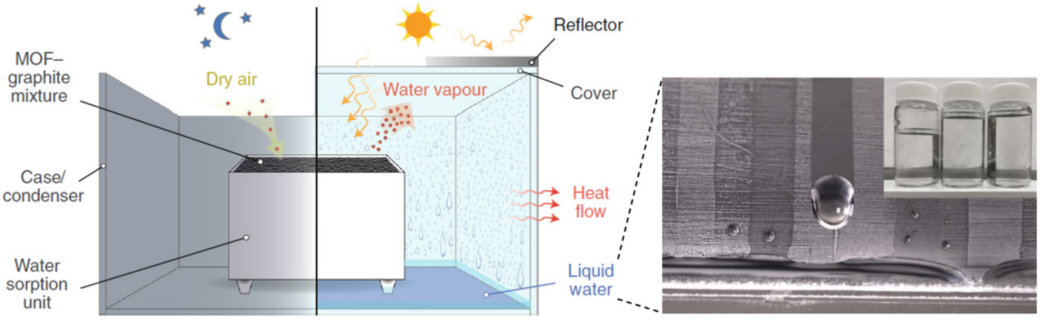

Fig. 4. Box-in-box design atmospheric water harvester. This device included 1.2 kg of MOF-801 and tested in Arizona dessert to demonstrate AWH capacity. Reproduced with permission from ref [18]. Licensed under the CC BY-NC.

the MOFs captured water from the air as the RH was higher than the inflection points of MOF-801. As the sun rose, the water-saturated MOF tray was covered by an outer box exposed to sunlight. Solar heating of the water harvester increased the MOF temperature to ~85°C, causing water molecules in the MOFs to desorb. Consequently, the RH in the box reached the dew point due to the increased water vapor concentration, initiating condensation and collecting drinkable liquid water. The latent heat released during condensation dissipated to the surroundings, facilitating the process of water desorption from MOFs and condensation on the inner surface of the box during the day cycles. Throughout these night-and-day cycles, water could be harvested from the desert air, where daytime RH was ~10% with temperatures of ~35°C. Importantly, this process occurred without using any external power, leading to carbon neutrality and demonstrating the significant potential of MOF-based AWH technology for both securing sustainable water and practicing carbon neutrality. In comparison to the theoretical water harvesting capacity of MOF-801 used, this device exhibited a ~25% water harvesting capacity (100g of water / kg of sorbents) in desert field tests.

6. The Most Recent Atmospheric Water Harvester Using MOF-303

While the simple prototype water harvester with a box-in-box design showcased the capability to harvest atmospheric water in arid climates using only natural energy, there were critical limitations to overcome for further scalable applications. The issue arose as the size of the sorbent beds increased, leading to a dramatic decrease in water capture efficiency due to the limited air accessibility of the sorbent bulk bodies. For instance, when using double the amount of MOF-801, the water harvesting capacity decreased by approximately 50% due to these reasons.

To address these challenges, Song *et al.* recently developed a scalable atmospheric water harvester capable of extracting atmospheric water even in extreme weather conditions (Fig. 5)[21]. This device adopted a cylindrical modular design that included MOF cartridge structures (Fig. 5A). Thanks to this distinctive and compact design, the entire MOF bodies in the cartridge could be efficiently exposed to the air, even with increased usage of MOFs. Notably, this device was the first to be developed based on systematic considerations of (1) MOF cartridge design for efficient water sorption-and-desorption during night and day cycles, (2) desorbed water vapor transport from the cartridge to the condenser, and (3) improving condensation rates at the condenser through surface modification. As a result, this harvester successfully extracted water from the air, even in one of the driest regions of the world, Death Valley desert in California, USA, during a three-day test in August 2022. Throughout this field test, the atmospheric temperature soared as high as ~58°C during the day, and the lowest RH was only

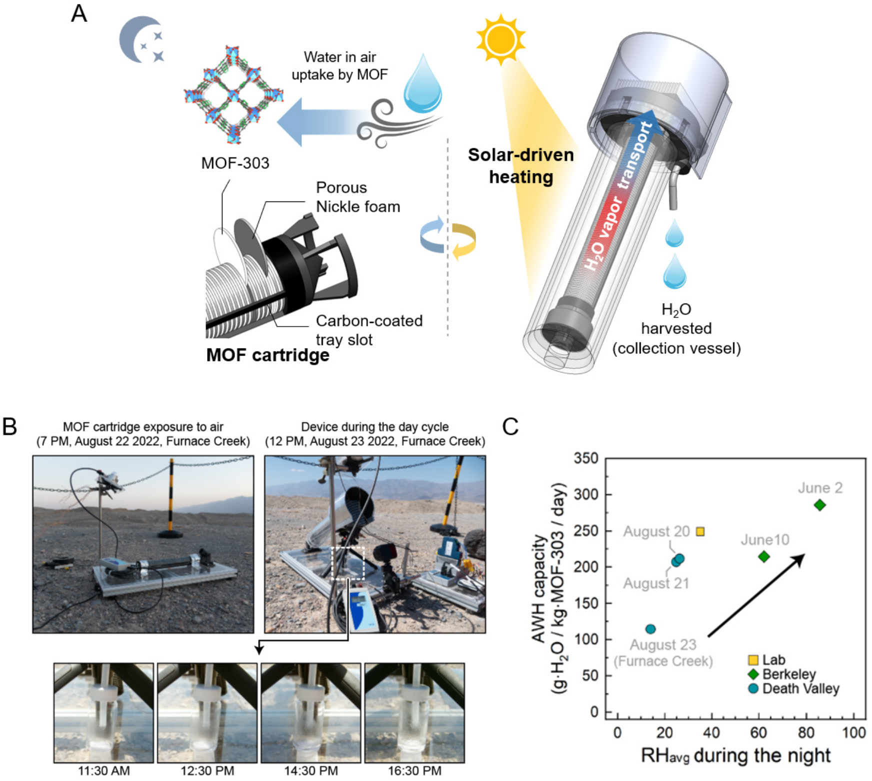

Fig. 5. Next-generation atmospheric water harvester. (A) Schematic drawings of the harvester to show water harvesting principles of the device. (B) Photographs of Death Valley field test during August, 2022. (C) AWH capacity of the device tested in different conditions. These figures were reproduced with the permission of ref [21]. Copyright© Springer Nature 2023.

~7%. Despite these extreme weather conditions, the harvester efficiently harvested water (Fig. 5B). In another field test conducted in the Berkeley area, this device achieved ~75% of water harvesting capacity (~290 g of water / kg of sorbents) compared to the theoretical capacity of MOF-303, demonstrating the impressive efficiency of the harvester even at a practical device scale (Fig. 5C).

7. Perspective on MOF-Based AWH and Membrane Technology

Combining atmospheric water harvesting technology using MOFs with membrane technology presents a promising approach to enhance water sustainability in arid and remote regions. By integrating MOF-based water adsorption and desorption systems with membrane technologies, a comprehensive water harvesting and purification solution can be achieved. For example, MOFs could be integrated into the hollow fibre membrane module format so that the surface area of water sorbent to air is maximized and therefore water capture efficiency becomes greater. Also, The MOF-based adsorption units capture water vapor from the atmosphere, concentrating it into a liquid phase. This concentrated water can then be further purified using membrane technology, removing any remaining impurities, contaminants, or salts to produce potable water. This integrated approach offers several advantages, including improved water quality, increased efficiency in water capture and harvesting, and the potential for decentralized water production in areas lacking traditional water infrastructure. Furthermore, by harnessing renewable energy sources for powering these systems, such as solar or wind energy, a sustainable and environmentally friendly water supply solution can be realized, contributing to addressing global water scarcity challenges. Ongoing research and development efforts are focused on optimizing the integration of MOF-based atmospheric water harvesting with membrane technologies to maximize water yield, energy efficiency, and scalability, thereby facilitating access to clean water for communities worldwide.

8. Conclusion

The recent progress and overview of MOF-assisted AWH research have provided valuable insights into the potential of this technology. While many studies are actively focused on developing new functional materials to enhance the efficiency of AWH technology, an equally crucial aspect is the integration of engineering expertise into this research field. The collaboration between material science and engineering disciplines becomes paramount to systematically design, develop, and optimize scalable and practical AWH devices and systems. By bridging the gap between material innovation and engineering implementation, researchers can address not only the material performance but also the broader challenges associated with deploying AWH on a large scale. This comprehensive approach ensures that the impacts of AWH technology can be effectively and sustainably brought into global communities, contributing to the solution of water scarcity challenges worldwide.

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