Supporting Information

MOF-integrated Bilayer Nanofibrous Membranes for Radiative-Cooling-Enhanced Atmospheric Water Harvesting

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Supplemental Notes

Supplemental Note 1. Calculation of thermal emissivity

To evaluate the cooling capability, the spectral emittance integrated over the atmospheric transparency window is quantified through the following expression equation (1):

$$\bar{\varepsilon}_{LWIR} = \frac{\int_{8\mu m}^{13\mu m} I_{BB}(T,\lambda) \cdot \varepsilon_{LWIR}(\lambda) d\lambda}{\int_{8\mu m}^{13\mu m} I_{BB}(T,\lambda) d\lambda} \quad \text{(Eq. S1)}$$

In this expression, $I_{BB}(T,\ \lambda)$ denotes the spectral radiance of a blackbody at a given temperature T, and $\varepsilon_{LWIR}(\lambda)$ signifies the spectral thermal emissivity of the surface at wavelength λ.

Supplemental Note 2. Calculation of net radiative cooling power

The net cooling power (P_{net}) of the sample can be estimated using the following equation:

$$P_{net}(T) = P_{rad}(T) - P_{atm}(T_{amb}) - P_{sun}(T) - P_{cond+conv} \quad \text{(Eq. S2)}$$

$P_{rad}(T)$ denotes the power density emitted by the radiative cooler via thermal radiation. $P_{atm}(T_{amb})$ represents the incident radiative power density originating from atmospheric thermal emission. $P_{sun}(T)$ is absorbed solar irradiation power, while $P_{cond+conv}$ is the non-radiative power density loss, accounting for both convection and conduction effects. $P_{rad}(T)$ can be derived from the measured spectral emittance of the sample by integrating it with the Planck distribution as follows:

$$P_{rad}(T) = \int d\theta \cos\theta \int_0^{\infty} I_{BB}(T,\lambda) d\lambda \varepsilon(\lambda,\theta) \quad \text{(Eq. S3)}$$

where $\varepsilon(\lambda,\theta)$ is the film's emittance and $I_{BB}(T,\lambda)$ is the spectral radiance of a blackbody at temperature of T according to Planck's law, which can be calculated using $I_{BB} = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/(\lambda K_B T)} - 1}$, h, c and κ_B represents the Planck's constant, the speed of light in vacuum and Boltzmann constant, respectively. $P_{atm}(T_{amb})$ is the power density of atmospheric thermal radiation absorbed by the cooler at T_{amb}, which is given by:

$$P_{atm}(T_{amb}) = \int \cos\theta d\Omega \int_0^\infty I_{BB}(T_{amb},\lambda)\varepsilon(\lambda,\theta)\varepsilon_{atm}(\lambda,\theta)d\lambda \quad \text{(Eq. S4)}$$

$\varepsilon_{atm}(\lambda,\theta) = 1 - \tau(\lambda)\frac{1}{cos\theta}$ is the angle-dependent emissivity of the atmosphere, $\tau(\lambda)$ represents the angular atmospheric transmittance.

$P_{sun}(T)$ attributed to solar loading is calculated by convolving the sample's spectral emittance with the AM1.5 global tilt solar irradiance, normalized to a total power density of 1,000 W m^{-2}.

$$P_{sun}(T) = \int_0^\infty d\lambda\varepsilon(\lambda,\theta_{solar})I_{AM1.5}(\lambda) \quad \text{(Eq. S5)}$$

$P_{cond+conv}(T,T_{amb})$ is the non-radiative heat exchange power, accounting for both convection and conduction, which can be expressed as:

$$P_{cond+conv} = h_c(T_{amb} - T) \quad \text{(Eq. S6)}$$

To evaluate both ideal and practical scenarios across various designs, the non-radiative heat transfer coefficient h_c was set at 0, 3, 6, 9, and 12 W m^{-2}K^{-1}.

Supplemental Note 3. Synthesis of MIL-101(Cr)

The experimental materials and detailed synthesis procedure of MIL-101(Cr) nanoparticles are given in the Supplementary methods. In a typical synthesis procedure, 10 g Cr (NO3)3·9H2O

(25 mmol), 1 g HF solution (20 mmol) and 180 g H2O (10 mol) were mixed and stirred until the crystals dissolved. The above solution was poured into 250 mL Teflon-lined stainless-steel autoclave, then 4.16 g 1,4-H2BDC (25 mmol) was added and heated at 220 ℃ for 10 h. The molar composition of the reactant mixture is 1 Cr3+: 1 H2BDC: 0.8 HF: 400 H2O. After natural cooling overnight, the suspension was centrifuged at 1000 rpm for 3 min to remove unreacted 1,4-H2BDC and then the supernatant liquid was centrifuged again at 6000 rpm for 10 min to obtain MIL-101(Cr). The synthesized MIL-101(Cr) was dispersed into excess DMF, washed by stirring at 120 ° C for 10 hours, and then centrifuged at 7000 rpm for 8 minutes. After this process was repeated for 3 times, MIL-101(Cr) was ultrasonically dispersed into water, frozen with liquid nitrogen and freeze-dried for 24 hours to obtain a well-dispersed dark green MIL-101(Cr) powder.

Supplemental Note 4. Preparation of PAN/MIL-101(Cr) NFM

PAN/MIL-101(Cr) NFM is prepared by electrospinning technology. First, 2 g of MIL-101(Cr) nanoparticles were added into DMF and then dispersed under ultrasonic treatment for 2 hours. Subsequently, 1 g (10 wt%) of PAN was added under magnetic stirring, and then 1 g of PVP was slowly added, and the mixture was vigorously stirred for 12 hours. The PAN/MIL solution was loaded into a plastic syringe, with the tip roller distance kept at 15 cm. The feed rate was 1 mL h^{-1}, the stable voltage was 16 kV, and the spinning process lasted 6 hours. The ambient temperature and RH were maintained at 23±1℃ and 46±3 RH%, respectively. The membrane was removed from the roller and immersed in 100℃ deionized water for 12 hours to remove PVP. Finally, the porous structure of PAN/MIL NFM was dried in a 100 ℃ oven.

Supplemental Note 5. Preparation of PAN/CB NFM

PAN/CB NFM was prepared by electrospinning technique. Briefly, 10 wt% of CB nanoparticles were added into DMF and then ultrasonic dispersed for 2 h. Subsequently, 10 wt% of PAN was added into the above solution. The blended solution was vigorously stirred for 12 h. Afterward, the electrospinning machine was applied, and the PAN/CB solution was transferred to a plastic syringes, and the tip-roller distance of 15 cm was maintained. The feed rate of 1 mL h^{-1} and a stable voltage of 20 kV were applied, and the spinning process lasted 4 h. The as-prepared PAN/CB NFM was deposited on a glossy paper covered roller. Finally, the black PAN/CB NFM was dried at 100 °C under vacuum.

Supplemental Note 6. Preparation of bilayer PM-PC NFM

The preparation of PAN/MIL NFM and PAN/CB NFM spinning solutions, as well as the spinning parameters, are presented as above. Notably, after 6 hours of PAN/MIL NFM spinning, it was directly replaced with PAN/CB spinning for 4 hours. Subsequently, the bilayer membrane was peeled off from the metallic roller and immersed in hot water at 100 ℃ for 12 hours to eliminate PVP. Eventually, the bilayer PM-PC NFM was dried in an oven at 100 ℃.

Supplemental Note 7. Optical Characterization

The reflectance across the solar spectrum (AM 1.5, ranging from 0.3 to 2.5 μm) was determined using a UV–Vis–NIR spectrometer (SolidSpec-3700, SHIMADZU, Japan). A $BaSO_4$ was employed as the reference material. The emissivity spectrum was acquired by measuring the reflectivity (R) within the range of 660 to 4000 cm^{-1} (equivalent to 2.5–15.2 μm) employing a Fourier transform infrared spectroscope (FTIR, Nicolet 6700, USA). Utilizing Kirchhoff's law, emissivity was calculated as 1-R considering negligible transmittance. A gold mirror was served as the reference standard throughout the measurement. Both measurement instruments were coupled with diffuse integrating spheres.

Supplemental Note 8. Outdoor radiative cooling and solar heating tests

To test the radiative cooling performance at night and the solar heating performance during the day, the samples were placed in a polystyrene foam box covered with aluminum foil to minimize heat conduction. A thin polyethylene film was applied on top of the box as a transparent window to reduce convective heat transfer. A T-type thermocouple thermometer was used to monitor the temperature changes of the samples and the environment, while a multi-channel data logger (TP700) recorded and stored the data. Humidity levels during the tests were monitored with a temperature-humidity recorder (TH10RS~TH22RS-EX), and solar irradiance was measured using a radiometer (YGC-TBQ).

Supplemental Note 9. Indoor water capture and release tests

The indoor water harvesting experiments were conducted in a temperature- and humidity-controlled chamber (HWS-80), where the ambient temperature (T_{amb}) and relative humidity (RH) were regulated. A thermoelectric device was used to maintain the sample temperature below T_{amb}. An electronic balance was employed to measure changes in the sample's mass. After each experiment, the sample was heated to restore its mass to the initial value before proceeding with the next test. For indoor water release experiments, a xenon lamp was used to simulate sunlight, and the changes in sample weight were recorded with an electronic balance.

Supplemental Note 10. Outdoor water capture and release tests

The outdoor water harvesting experiments were conducted in 2024. All test samples had similar initial masses and were placed on foam to prevent heat conduction. Aluminum foil shields were used to eliminate radiative cooling effects while allowing airflow. A T-type thermocouple was used to measure the temperature at the bottom of the samples, and a temperature-humidity recorder (TH10RS~TH22RS-EX) monitored the RH. An electronic balance recorded changes in the

samples' mass. The outdoor water release experiments were also performed in 2024. The samples were exposed directly to sunlight, and a solar radiometer (YGC-TBQ) was used to measure the solar irradiance.

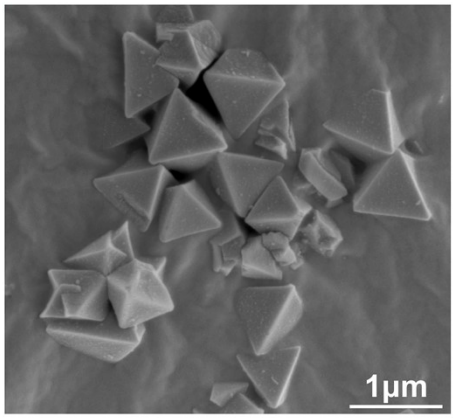

Figure S1. Scanning electron microscope image of MIL-101 particles.

Figure S2. Size distribution of MIL-101 particles.

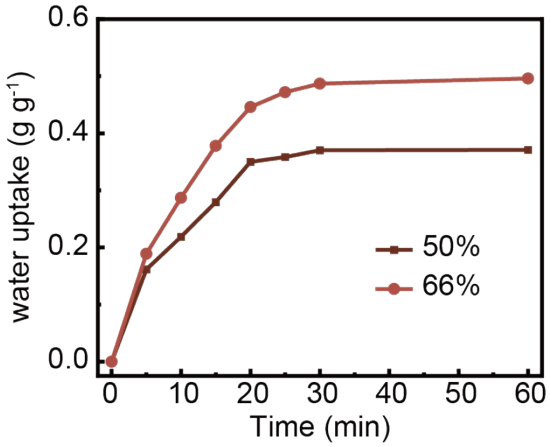

Figure S3. Comparison of water uptake over time for membranes with 50% and 66% MIL-101 loading.

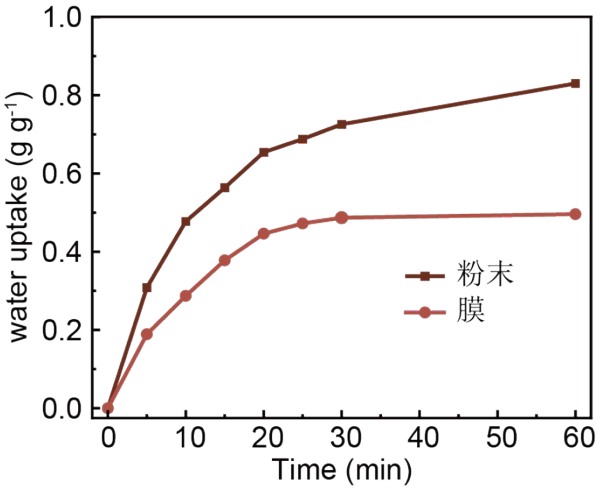

Figure S4. Water uptake over time for MIL-101 powder and the PM-PC nanofibrous membrane.

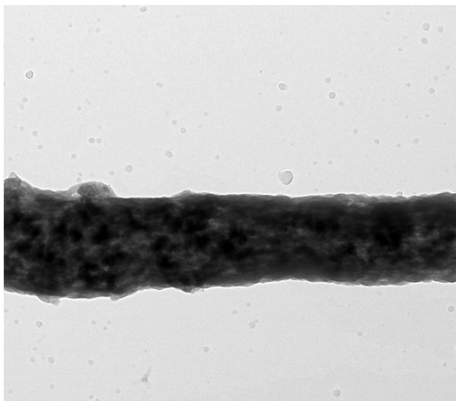

Figure S5. Transmission electron microscope image of PAN/CB.

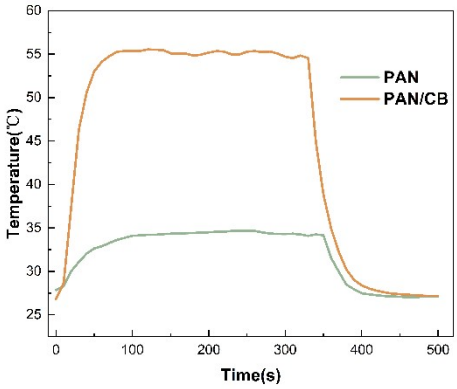

Figure S6. Surface temperature curves of PAN and PAN/CB membranes under 0.5 sun irradiation.

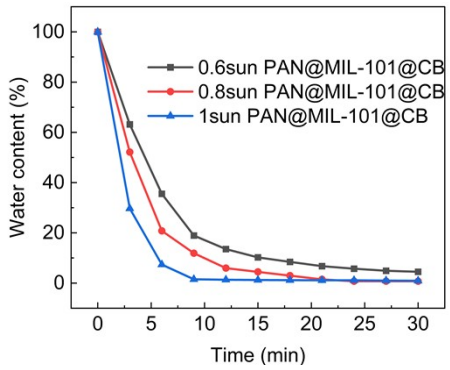

Figure S7. Comparison of solar-driven water desorption kinetics of the PAN@MIL-101@CB membrane under various solar intensities (0.6, 0.8, and 1.0 sun).

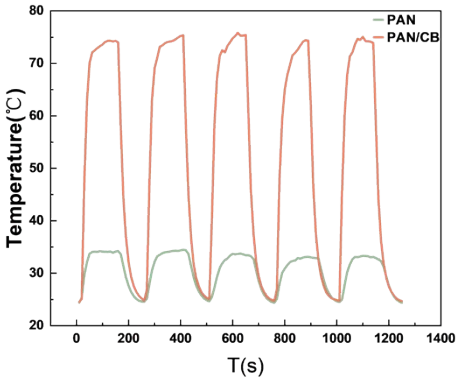

Figure S8. Photothermal cycling stability of the PAN/CB membrane over five consecutive light-on/off cycles.

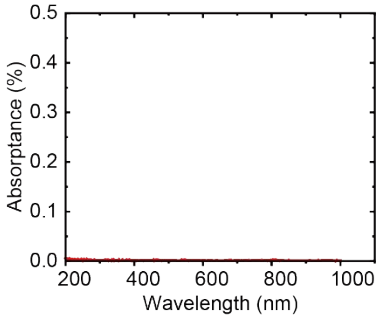

Figure S9. UV–Vis absorption spectrum of water collected by the membrane.

Table 1. Metal test in water collected by the membrane.

	Concentration average(ppm)	GB 5749-2022 (ppm)
Al	0.12	0.2
Mn	0.001	0.1
Cr	0.004	0.05
Zn	0.024	1
Cu	0.007	1