Phospholipid Bilayer Inspired Sandwich Structural Nanofibrous Membrane for Selective Water Harvesting and Release

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Abstract

Atmospheric water harvesting (AWH) has been broadly exploited to meet the challenge of water shortage. Despite the significant achievements of AWH, the unendurable water harvesting, inferior water release performance, and short service life hinder practical applications. Herein, inspired by the unique selective permeability of the phospholipid bilayer, a sandwich structural polyacrylonitrile nanofibrous membrane (San-PAN) was fabricated to improve the water sorption/desorption ability. The special wettability of the sandwich structure (hydrophobic-hydrophilic-hydrophobic) could confine the captured water in the hydrophilic layer and prevent the leakage of the hygroscopic salt, achieving continuable and recyclable water sorption/desorption. Notably, attributed to the high thermal conductivity of Ag particles in the inner layer, the water condensation, and heat transfer ability of San-PAN were remarkably enhanced. As demonstrated, the as-prepared AWH devices presented a high-efficient adsorption kinetics (4.08 g g\(^{-1}\) at 25°C and 90% relative humidity). Thus, this work strengthens the understanding of the water sorption/desorption process and opens an avenue to the practical applications of wearable outdoor water supply equipment.

Introduction

Water shortage is an urgent worldwide challenge for humans, especially in arid and semi-arid lands.\(^1\),\(^2\) It is estimated that over the next 30 years, more than half of the world’s population will face a shortage of clean water.\(^3\),\(^4\) To cope with this challenge, some functional materials and ingenious devices have been fabricated for fog collection,\(^5\),\(^6\),\(^7\) rainwater collection,\(^8\),\(^9\) seawater desalination,\(^10\),\(^11\),\(^12\) and filtration,\(^13\) etc. It is worth noting that the atmospheric water in the air contains abundant water molecules and can be regarded as a promising resource for dealing with water challenges.\(^14\),\(^15\),\(^16\) The cost-effectiveness, low energy consumption, and continuous water production under the low RH conditions enable (atmospheric water harvesting) AWH to attract significant attention.\(^17\),\(^18\),\(^19\)

To address the challenges of effective and continuous AWH, there are a few aspects that need to be considered: (1) continuous water molecules absorption, (2) rapid water desorption, and (3) recyclability and recoverability of the AWH devices.\(^20\),\(^21\) For now, great efforts have been applied to develop highly effective water absorption materials (Metal-Organic Framework (MOF),\(^22\),\(^23\) Covalent-Organic Framework (COF),\(^24\) hydrogels\(^25\) and organogels,\(^26\) etc.) and match with photothermal devices. As frequently-used materials for AWH, LiCl and CaCl\(_2\) particles were popular due to their highly effective performance and economical. However, the recyclability and recoverability of the hygroscopic salt still hinder the practical application of AWH due to the leakage of salt solution during water sorption/desorption cycles.\(^27\)

Some porous materials such as nanofibrous membranes,\(^28\),\(^29\) textiles,\(^30\) hydrogels,\(^31\) and aerogels\(^32\) were employed as a carrier to confine salts. Owing to the strong capillary force of the micropores, the salt solution would be confined in the carriers.\(^33\) However, the confined pore size limited its water uptake ability. The salt solution would leak again when the carriers were exposed to a moist environment for a
long time where the captured water was too much to be stored inside the pores. Some efforts are devoted to developing a porous matrix with ultrahigh pore volume to uptake salts and keep the salt solution as much as possible. But the volume of the porous matrix was confined, and the water uptake ability of the ultrahigh pore volume was still limited. Fortunately, some subtle structures in nature have brought us new inspirations. The phospholipid bilayer on the cell membrane has a special wettability structure (hydrophilic-hydrophobic-hydrophilic), making it selectively permeable. The special wettability structure allows only some substances (such as glucose, carbon dioxide, etc.) to pass through. In contrast, other substances (such as proteins) aren’t allowed to pass through or only partially can pass with the help of certain conditions.

Inspired by the selectively permeable phospholipid bilayer of the cell membrane, a sandwich structural nanofibrous membrane (San-PAN) was prepared using an electrospinning and impregnation method for AWH. The inner layer (CB-Ag-LiCl@PAN) was the moisture absorption layer loaded with hygroscopic LiCl for highly efficient AWH. Furthermore, in situ Ag deposition endows the CB-Ag-LiCl@PAN with high thermal conductivity and antibacterial properties, which accelerates the condensation and evaporation rates of the water, and improves the safe portability of the collected water. The outer layers (top layer and bottom layer, CB-PDMS@PAN) were modified by PDMS to achieve hydrophobicity, which can selectively allow the permeation of water molecules but prevent the leakage of collected salt solution. The LiCl enabled the San-PAN a significant water uptake rate of about 4.08 g g$^{-1}$ at 90% relative humidity (RH) under room temperature ($25^\circ$C). CB particles combined with the Ag coating contributed to rapid photothermal conversion and heat transfer of the San-PAN. Under 1.0 sunlight conditions, the saturated San-PAN released all the captured water in 25 min. With fast moisture absorption and transport rates, superior long-term stability, and excellent lightweight and flexible mechanical properties, the San-PAN shows potential value in commercial outdoor clothes for continuous water production.

**Results And Discussion**

**Design of sandwich structural PAN nanofibrous membrane**

The phospholipid bilayer of the cytomembrane displays well-designed structures where the hydrophilic head of the phospholipid molecule is on the surface of the membrane, and the hydrophobic tail is on the interior of the membrane. The sandwich structural wettability (hydrophilic-hydrophobic-hydrophilic) membrane enables the cells to selectively absorb nutrients needed for life activities (Fig. 1a). Inspired by the phospholipid bilayer, a sandwich structural wettability (hydrophobic-superhydrophilic-hydrophobic) PAN nanofibrous membrane (San-PAN) was fabricated for water absorption and selectively water release.

As demonstrated in Figure. 1b, the San-PAN consists of two hydrophobic membranes at both ends of the sandwich structure, while the hydrophilic layer is located in the center. Firstly, the CB@PAN was prepared by electrospinning PAN/CB mixed solution and then impregnated CB@PAN into PDMS solution to fabricate the hydrophobic layer (CB-PDMS@PAN). The inner layer (CB-Ag-LiCl@PAN) was prepared by in
situ Ag deposition of CB@PAN and then immersed into 30 wt% LiCl solution. Finally, stack the three membranes (CB-PDMS@PAN, CB-Ag-LiCl@PAN, and CB-PDMS@PAN) together from top to bottom, and a sandwich structural water-harvesting device was successfully prepared. The ingenious design could achieve effective AWH and selective water vapor release. The captured liquid water would be stored inside the layer without any leakage. Under solar irradiation, the liquid water would evaporate in the vapor phase (Fig. 1c). Without the protection of the outer hydrophobic layer, the inner layer (CB-Ag-LiCl@PAN) captured water would leak rather than a store (Fig. 1d). A schematic illustration of the water sorption/desorption process of the San-PAN was exhibited in Fig. 1e. With high humidity, such as in the evening, the inner layer (CB-Ag-LiCl@PAN) would capture the water molecules due to the presence of hygroscopic LiCl and the excellent condensation properties of Ag particles. However, when the sunlight directly irradiated the San-PAN, the existence of the CB particles enabled the outer layer (CB-PDMS@PAN) to convert the light energy to heat energy. Ag particles transferred heat from the outer surface to the inner layer, achieving highly efficient water evaporation.

The surface morphologies of the PAN, CB@PAN, CB-PDMS@PAN, and CB-Ag-LiCl@PAN were characterized by scanning electron microscopy (SEM, Fig. 2a-d). The original PAN fibers were uniform and smooth, with an average diameter of 0.5 µm (Fig. 2a). After doping with carbon black, numerous nanoparticles were decorated on the as-prepared CB@PAN (Fig. 2b). Subsequently, the surface of the CB-PDMS@PAN became smooth after modifying with low surface energy PDMS. It was clear that CB nanoparticles were anchored on PAN fiber and wrapped with a PDMS coating (Fig. 2c). The chemical groups of CB@PAN and CB-PDMS@PAN were characterized by the FT-IR spectrum (Figure S1). After PDMS modification, new peaks emerged in 2964 cm$^{-1}$ (CH$_3$), 1205 cm$^{-1}$ (Si-C), 866 cm$^{-1}$ (Si-CH$_3$), 755 cm$^{-1}$ (C-H), 1022 cm$^{-1}$ and 845 cm$^{-1}$ (Si-O-Si). Figure S2 showed the distribution mapping images of elements Si and C. Many Si elements were distributed on the sample's surface, indicating that PDMS has modified the sample. Meanwhile, the surface morphologies and chemical structures of the inside layer (CB-Ag-LiCl@PAN) were also characterized. After in situ silver mirror reaction, the CB-Ag@PAN fiber was decorated with Ag particles and became rough (Figure S3). Sequentially, after the CB-Ag@PAN were impregnated into the LiCl solution to obtain the CB-Ag-LiCl@PAN, the SEM images of the CB-Ag-LiCl@PAN showed plenty of deposited LiCl particles, and the pores were almost completely filled (Fig. 2d). The chemical element distribution (C, Cl, and Ag) of the CB-Ag-LiCl@PAN was exhibited in Figure S4. The elements proportions of Cl (56.47%) and Ag (20.27%) indicated that the Ag and LiCl were successfully distributed on the CB-PDMS-LiCl@PAN. The Ag and LiCl were covered entirely on the surface of CB-PDMS-LiCl@PAN, resulting in difficulty detecting the original PAN fiber. Thus, the atomic contents of C and N were only 20.78% and 2.48%, respectively (Figure S5). X-ray diffraction (XRD) data of the characteristic peaks of Ag (44.765, 65.166, 82.531) and LiCl (31.458) were strongly indicated the existence of Ag, while there was no distinct peak that can be found in the CB@PAN. The diffraction patterns of the CB-LiCl@PAN and CB-Ag-LiCl@PAN closely matched that of Ag particles, revealing the existence of well-defined Ag and the amorphous structure of LiCl in the CB-Ag-LiCl@PAN.$^{28}$
Due to the numerous macroscopic holes, the CB@PAN exhibited rapidly diffused and infiltrated water absorb ability, the whole water infiltrated time lasted 3.25 s (Figure S6). After being coated with PDMS, the CB-PDMS@PAN obtained hydrophobicity with a contact angle of about 132.5° (Fig. 2e). Even under the pressure of 500 mL of liquid water, the CB-PDMS@PAN could prevent the water's penetration, showing good hydrophobicity and mechanical strength (Figure S7). As for CB-Ag-LiCl@PAN, the deposited hygroscopic LiCl particles enabled the CB-Ag-LiCl@PAN a superior hydrophilicity. It only takes 2.16 s for the sample absorbed the water (Fig. 2f).

However, owing to the strong AWH ability of LiCl particles, the San-PAN remained in a moist state, resulting in the potential for bacterial growth and biological corrosion. The anti-adhesion ability of CB-LiCl@PAN and CB-Ag-LiCl@PAN against bacteria was evaluated in Figure S8. Gram-negative bacteria- *E. coli* was chosen as a target in the whole experiment. After co-incubation at 37°C for 24 h, a large number of E. coli colonies were grown on the plate of blank sample, and the CB-LiCl@PAN, approximately 3000 and 460 bacteria adhered on a 10 cm² of LB agar plate, respectively. In contrast, almost no E. coli colonies were grown on the CB-Ag-LiCl@PAN, indicating outstanding antibacterial performance. The antibacterial rate of CB-Ag-LiCl@PAN was significantly up to 99.97%, indicating the inherent antibacterial capability of CB-Ag-LiCl@PAN, which meets the requirement of WHO for drinking water (Figure S9).

Additionally, the pore size of the CB-PDMS@PAN (out layer) were an important factor for the rapid water molecules transmission. The pore size of the CB-PDMS@PAN should be confined in a certain range. If the pore size of CB-PDMS@PAN was too small, it would prevent the free passage of the water molecules, and the minimum pore size was determined by the mean free path of a water molecule (\(\lambda\): the average of the possible free paths of a water molecule between two successive collisions under certain conditions), as following Eq. (1):\(^{40}\)

\[
\lambda = \frac{\bar{v}}{Z} = \frac{1}{\sqrt{2\pi d^2 n}}
\]

1

Where \(d\) is the water molecule's effective diameter (0.4 nm), \(n\) represents the density of the number of molecules, and since the pressure, \(P = nkT\) (\(k\) is the Boltzmann constant \(1.38 \times 10^{-23} \text{ J/K}\) and \(T\) is the temperature \(298.15\text{K}\)), the mean free path can be obtained by the following Eq. (2):\(^{40}\)

\[
\lambda = \frac{kT}{\sqrt{2\pi d^2 P}}
\]

2

where \(P\) represents the standard atmospheric pressure, which is \(1.01 \times 10^5 \text{ Pa}\), the diameter of water molecule is 0.4 nm. By theoretical calculation and analysis, the mean free path of a water molecule is
about 57 nm. On this basis, to achieve the free transmission of the water molecules, the pore size of aerogel should be greater than 57 nm.

However, unlimited enlarge of pore size will lead to droplet leakage. The maximum critical value of pore size is determined when the water surface tension and hydrostatic pressure was equal (Figure S10, Eq. 3):

$$\sigma \pi d \times \cos \theta = \rho g h \times \pi (d/2)^2$$

Where $\sigma$ is the surface tension of water ($\sim 0.072 \text{ N/m}$), $h$ is the depth of water (in San-PAN, the depth could be regarded as 0.01 m), $\theta$ is the contact angle ($\sim 130^\circ$) of the aerogel and $d$ is the maximum pore size of the aerogel. As illustrated, the calculated maximum pore size of the CB-PDMS@PAN is $\sim 1.8 \text{ mm}$. As discussed above, the pore size of the CB-PDMS@PAN should be confined between 57 nm and 1.8 mm to enable free transmission of water molecules and prevent leakage of liquid water.

The pore size of the CB@PAN and the CB-PDMS@PAN were presented in Fig. 2g. Typically, the pore size of the CB-PDMS@PAN (about 9–11 µm) was slightly smaller than that of the CB@PAN (about 10–11 µm). The appropriate pore size (9–11 µm) of the CB-PDMS@PAN enables it to transport water molecules ($\sim 0.4 \text{ nm}$) selectively but prevents liquid water from leaking. Figure 2h exhibited the water transmission rate of the PAN, CB@PAN, and CB-PDMS@PAN. With a 90% RH at 25°C, the water transmission rate of the CB-PDMS@PAN was 6.3192 kg day$^{-1}$ m$^{-2}$, slightly lower than that of the PAN (7.3440 kg day$^{-1}$ m$^{-2}$) and the CB@PAN (6.9720 kg day$^{-1}$ m$^{-2}$) (Fig. 2h). The above result indicates that the CB and PDMS coating did not affect water transmission. The reason could be attributed to the massive micron-sized interwoven pores were not changed by the tiny CB particles and thin PDMS coating.

**Water absorption test**

As the San-PAN place in the environment, it could continuously absorb the water molecules in the air. The water absorption mechanisms were as follows (Fig. 3): (1) Chemisorption by noncovalent interaction between hydrophilic functional groups and water molecules. Small amounts of -OH and -COOH contains in CB particles. These hydrophilic functional groups possess lone-pair electrons and vacancies, were the the donor and acceptor for surrounding water molecule to form hydrogen bonds. When exposed in the air, these hydrophilic functional groups bond with water molecules through hydrogen bonds or electrostatic interaction, enable the San-PAN via noncovalent interaction to capture the water molecules. (2) Single-layer and multi-layer adsorption. With the increase of water vapor partial pressure on the surface of San-PAN, the physical adsorption behaviour of adjacent water vapor molecules combined with the water absorbed by the previous layer is multi-layer adsorption dependent on van der Waals force. The water captured by multi-layer adsorption exists between the water captured by the hydrophilic functional group of HPPs and the free water captured by the subsequent adsorption, which is generally called intermediate water. (3) Capillary condensation in the nano porous structure. Nanofibrous membrane is a typical porous
material. According to the Kevin equation, when the critical pore diameter is reached, the water vapor can be condensed in the capillary channel even if the partial pressure of water vapor is lower than the saturation value.\(^4\) (4) Chemisorption by covalent interaction between hygroscopic factors and water molecules. A great amount of LiCl particles were deposited in the nanofibrous membranes, the Li\(^+\) capture bits of water molecules and form coordination bonds between salt crystal's vacancies and water molecules. Further, the continuous water harvesting process induces the solvation process of salt crystals, which indicates that subsequent absorbed water interacts with LiCl, both anions and cations by ionic bonds, hydrogen bonds, and electrostatic interactions. With the formation of a stable hydration layer, consecutive water vapor is captured by the concentrated salty solution until the water vapor’s partial pressure on the salty solution's surface is equal to on the ambient’s.

The water absorption ability of the San-PAN was gravimetrically evaluated at 25 °C with different relative humidity. If not otherwise specified, the relative humidity of the tests was 90%. As we all know, metal Ag has rapid thermal conductivity (429 W (m·K)\(^{-1}\)). To clarify the significance of Ag deposited on CB-LiCl@San-PAN, the water uptake rate of the San-PAN before (CB-LiCl@San-PAN) and after (CB-Ag-LiCl@San-PAN) Ag deposition was compared. As shown in Fig. 4a, the water molecules condensed faster in the CB-Ag-LiCl@San-PAN with time. Ultimately, the CB-Ag-LiCl@San-PAN led to a higher uptake rate (4.08 g g\(^{-1}\)) than that of the CB-LiCl@San-PAN (3.76 g g\(^{-1}\), thermal conductivity: 0.051 W (m·K)\(^{-1}\)). The higher thermal conductivity of the deposited Ag and the hygroscopicity of dispersed salt are the two main factors for CB-Ag-LiCl@San-PAN to achieve significant moisture adsorbing ability.

As observed in Fig. 4b, the water absorption capacities of dried CB-Ag-LiCl@San-PAN at 30%, 60%, and 90% RH reached 1.66, 2.68, and 4.08 g g\(^{-1}\), respectively. It took only 120 min for CB-Ag-LiCl@San-PAN to arrive at moisture balance. The water uptake rate was positively related to the increasing RH because more water molecules could combine with active sites of LiCl particles. Moreover, the faster water uptake rate under the higher humidity takes a shorter time for the samples to reach equilibrium. Owing to the well-designed structures and novel strategy, the addition of LiCl enabled the CB-Ag-LiCl@San-PAN with significant hygroscopicity, and the massive micron-sized interwoven pores accelerated the water permeation and diffusion. Notably, LiCl particles reduced the water vapor pressure on CB-Ag-LiCl@San-PAN. The higher thermal conductivity of Ag coating was conducive to water molecules’ condensation.

The moisture absorption stability is necessary for a water-harvesting device in practical applications. Figure 4c exhibited the water uptake ability of the San-PAN and CB-Ag-LiCl@PAN (Sin-PAN) during 10 cycles. The water uptake rate of San-PAN remained at ~ 3.88 g g\(^{-1}\), while Sin-PAN sharply declined from ~ 4.08 g g\(^{-1}\) to ~ 0.78 g g\(^{-1}\) during 10 cycles. Meanwhile, the LiCl uptake rate of the San-PAN remained at a high level while Sin-PAN was significantly reduced from ~ 0.82 g g\(^{-1}\) to ~ 0.19 g g\(^{-1}\). The distinct difference in cyclic water absorption between San-PAN and Sin-PAN could be contributed by the water sorption ability of LiCl. Figure 4d illustrated the whole water molecules’ absorption process of LiCl particles. Under constant RH, the water molecules were first physically absorbed by the San-PAN with massive micron-sized interwoven pores. Then, the LiCl particles attached to the inside of the pores.
undergo a chemical adsorption process with water vapor to form hydrated salts. The whole hydration process could be divided into two steps and presented in the form of LiCl·nH$_2$O crystalline salt. With the continuous inhalation of water vapor into the pores, the internal hydrated salt further absorbs water and hydrolyses. First, a liquid film of saturated salt solution was formed on the surface of the hydrated salt particles. As the hydrated salt continuously absorbed the water molecules, it dissolved and formed a saturated salt solution. As water molecules continued to be absorbed, the concentration of the saturated salt solution would gradually decrease, forming a dilute saline solution.

The process of water absorption and leakage for the Sin-PAN and San-PAN was exhibited in Fig. 4e, f. When the Sin-PAN was applied, many water molecules were captured, and the saline solution appeared in the Petri-disk. However, the excess saline solution would leak out from the nanobrous membrane with a further increase in water absorption. The leakage of saline solution would cause the decrease of LiCl particles in Sin-PAN, which may affect the uptake rate in the next cycle (Fig. 4e). To solve the leakage issue, hydrophobic CB-PDMS@PAN nanofiber membrane was used as a barrier layer on the top and bottom of the CB-Ag-LiCl@PAN, respectively, regarded as San-PAN (Fig. 4f). No obvious liquid came out from the San-PAN surface after 2 h, meaning no leakage happened on the San-PAN. As illustrated in Fig. 4g, the water absorption process of San-PAN could contribute to the synergistic effect of the water harvesting property of hygroscopic LiCl particles and the rapid water condensation ability of Ag particles.

To prove the rationality of San-PAN for water absorption, the water absorption rate was quantitatively compared with previously reported advanced materials and devices (Figure S11). The San-PAN presented a significantly higher water sorption rate at different humidity than other reports. As a result, the San-PAN could be widely used for practical applications and as a long-time water-harvesting material, surpassing the performance of other granular solid desiccant materials.

**Water desorption test**

Apart from the water sorption, the desorption abilities also affect the final water collection rate. To gain clean water from the captured saline solution, CB particles with high photothermal performance were loaded on the nanofiber to achieve rapid water vapor evaporation. In a standard solar spectrum, the CB@PAN with an 8 wt% CB loading exhibited a solar absorption rate of up to 97% within the wavelength range from 400 to 2500 nm, significantly higher than the original PAN (Fig. 5a). Surface roughness and surface area would affect the full-wave band absorptance. Roughness surfaces could refract and reflect the light source multiple times, which decreased the light reflectance and enhanced the light absorbance. And also, a larger surface area could capture more light sources to transform into heat.

Figure 5b showed the initial temperatures of the San-PAN with CB coating (CB@San-PAN) and without (CB@San-PAN) were similar before solar irradiation. However, the surface temperature of the CB@San-PAN rapidly increased to 96.5°C after 50 min treatment under simulated illumination of 1 kW m$^{-2}$. The rapid heating rate could be attributed to the photothermal properties of carbon black loaded on the CB@San-PAN, which exhibited potential for solar-driven water evaporation. On the contrary, the maximum
temperature the ORI@San-PAN surface could reach is only 45.2°C without CB loading. The cumulative mass changes of the ORI@San-PAN and CB@San-PAN were tested under solar irradiation to evaluate the evaporation rate. During the first 20 min, the mass of captured water for CB@San-PAN sharply descended and tended to be stable (Fig. 5c). The CB@San-PAN exhibited a significantly rapid water evaporation rate and fast water desorption within a short time. It took 25 min for saturated CB@San-PAN to dry out the captured water, whereas it was about 60 min for the saturated ORI@San-PAN under solar irradiation. The evaporation rate of these two samples was calculated in Figure S13. After 15 min of solar irradiation, the highest evaporation rate of the CB@San-PAN reached ~ 0.176 g (g min)^{-1}, which was higher than that of ORI@San-PAN (~ 0.067 g (g min)^{-1}). Therefore, the rapid water evaporation rate of CB@San-PAN further proved CB particles’ superior light absorption ability.

Essentially, the outer layer could be directly illuminated by a light source while the inner layer could not. It must be noted that there was a significant temperature difference between the outer layers and inner layer. As shown in Fig. 5d, the highest temperature of the outer layer (CB-PDMS@PAN) could reach 95.6°C, while the inner layer (CB-LiCl@PAN) was 76.4°C. However, since the captured water was distributed in the inner layer, the temperature in the inner layer should be increased. It is of great significance to enhance the thermal transfer from the outer to the inner layer to accelerate the inner water evaporation. As discussed above, we adopted an electroless Ag plating method in situ deposition of Ag particles on the inner layer (CB-Ag-LiCl@PAN). After Ag deposition, the CB-Ag-LiCl@PAN exhibited a remarkably high thermal conductivity (429 W (m·K)^{-1}) than that without Ag deposition (0.051 W (m·K)^{-1}). As shown in Fig. 5e and f, benefiting from the enhanced thermal conductivity of the deposited Ag particles, the CB-Ag-LiCl@PAN demonstrated a rapid temperature increase rate (only costs 45 min to reach the max temperature). The max temperature could arrive at 85.7°C. The saturated sample could be dried out within 25 min. However, for the inner layer (CB-LiCl@PAN) without Ag deposition, its max temperature was only 76.4°C and took 35 min to evaporate the water in the saturated sample. The max water evaporation rate of these two samples (CB-Ag-LiCl@PAN: 0.176 g (g min)^{-1}, CB-LiCl@PAN: 0.141 g (g min)^{-1}) further illustrated the reasonable of the deposited Ag particles on the inner layer (Figure S14).

With a high broadband solar absorption (CB particles loading), rapid water molecules transfer (hydrophobic-hydrophilic-hydrophobic wettability), and good moisture permeability (micropores of nanofibrous membranes), the San-PAN (outer layers: CB@PAN, inner layer: CB-Ag-LiCl@PAN) achieved fast photothermal conversion and rapid water evaporation under one-sun illumination. To exhibit the significance of the photothermal and heat transfer ability of San-PAN, the surface temperature distributions of the inner layer and outer layer under one-sun illumination were recorded by an infrared (IR) thermal camera (Fig. 5g and h). The initial surface temperature of the outer layer (24.4°C) and the inner layer (24.3°C) was similar before illumination. As the light source continued to illuminate the San-PAN, the surface temperature of the outer layer rapidly increased within a few minutes and reached 96.5°C. With the rapid heat transfer ability of Ag coating, the inner layer could be headed to 85.7°C. Figure 5i demonstrates the photothermal conversion and heat transfer processes of the San-PAN under solar irradiation. The CB particles loaded on the outer layer (CB-PDMS@PAN) would firstly convert the
light source to the thermal source, and the Ag deposited on the inner layer could rapidly transfer the heat from the outer layer (CB-PDMS@PAN) to the inner layer (CB-Ag-LiCl@PAN).

Practical outdoor AWH demonstration and application models

To further investigate practical applications of the San-PAN for water collection, the experiments were conducted in a practical outdoor environment by using self-made equipment (19:00, June 24 to 19:00, June 25, 2022, Wuxi, China). The San-PAN was placed in an electronic balance to measure the mass change (Fig. 6a). Under the solar irradiation, the adsorbed water in the San-PAN vaporized and dropwise condensed on the transparent acrylic box. The condensed water droplets were first nucleation, grown, and finally dropwise rolled down, collected at the bottom of the acrylic box. Figure 6b and c presented the optical images of the collected water and solar flux. The results of the inductively coupled plasma mass spectrometry (ICP-MS) test manifested that the collected water met the drinking water requirements of the World Health Organization (WHO) and the US Environmental Protection Agency (EPA) (Figure S12). Figure 6d presented the outdoor water sorption/desorption ability of the San-PAN, where the environmental temperature and RH were recorded in Fig. 6e. During the night (19:00 to 5:00), the dried San-PAN was applied for water absorption with the highest water uptake rate at ~ 4.05 g g\(^{-1}\). During the daytime (5:00 to 19:00), the saturated San-PAN was put in a transparent acrylic box for evaporating under solar irradiation. During the whole water sorption/desorption process, about 3.1 g of water was collected at the bottom of the box.

With the remarkable water production and flexible mechanical properties of the well-designed San-PAN, we expected to explore a broad range of applications of such a bio-inspired sandwich structural nanofibrous membranes water collector and proposed a brand-new application model (Figs. 6f and g). As a proof-of-concept product, the San-PAN could be used as water supply equipment for outdoor sports. Compared to the frequently-used kettle (weight of 2000 g), the San-PAN could be carried as a cloth accessory with a weight of ~ 1 g and continuously produce fresh drinking water. This application concept of the well-designed San-PAN would reduce outdoor sports personnel's burden, enabling weightless outdoor sports to come true.

Conclusion

Taking inspiration from the selective permeability of phospholipid bilayer, a sandwich structural nanofibrous membrane (San-PAN) was fabricated via electrospinning and impregnation method. Further research through water sorption tests instructed the optimization strategy of the sandwich wettability design (hydrophobic-hydrophilic-hydrophobic), revealing the importance of heterogeneous wetting properties for recyclable water sorption/desorption. Remarkably, the hydrophilic layer (CB-Ag-LiCl) with in situ Ag coating exhibited a magnificent thermal conductivity and achieved efficient water condensation and heat transfer, enhancing water collection and evaporation. The San-PAN showed the highest water
uptake value of 4.08 g g$^{-1}$ and did not change after 10 cycles. Remarkably, based on the photothermal properties of doped CB particles and thermal conductivity of deposited Ag coating, the water on the saturated San-PAN could be completely evaporated within 25 min under 1.0 solar intensity. This well-designed San-PAN with excellent water harvesting efficiency and selective water release ability showed the promise for large-scale water harvesting. We envision that such a flexible, light, and superhygroscopic San-PAN with continuous water production ability will provide new opportunities for AWH materials in outdoor equipment for water supply.

**Experimental Section**

**Materials**

Polyacrylonitrile (PAN) and carboxylation carbon black (CB) were commercially available from a local market. Lithium chloride (LiCl), N,N-dimethylacetamide (DMF), n-hexane (analytical reagent grade), AgNO$_3$, ammonium hydroxide (NH$_4$OH), NaOH, glucose, and methylene blue were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). PDMS (Dow Corning 184A) and the curing agent (Dow Corning 184B) were purchased from Dow Corning.

**Fabrication of sandwich structural PAN nanofibrous membrane**

(1) Preparation of the CB@PAN

The superhydrophilic PAN (SHL PAN) nanofibrous membrane was fabricated through the electrospinning technique. The lab-made electrospinning equipment includes a pump, injector, and a rotating drum connected with an electrode. First, 10 wt% of PAN was dissolved in the DMF solution for 12 h with mechanical stirring. 8 wt% of CB nanoparticles were added into the as-prepared solution and dispersed in an ultrasonic machine for 6 h, regarded as a spinning mixture. Then, 3 mL of the spinning mix was added to the injector with a constant extrusion speed of 1.5 mL h$^{-1}$. The applied voltage was 20 kV, and the distance between the injector and the collector was 20 cm. The rotation speed of the collector was maintained at 40 rpm min$^{-1}$. After spinning for 2 h, the CB@PAN was obtained.

(2) Preparation of the CB-PDMS@PAN

2 wt% of PDMS ($m_{\text{pre-pol}}:m_{\text{curing agent}} = 10:1$) was dissolved in n-hexane for 6 h with mechanical stirring to obtain a hydrophobic agent. The CB-PDMS@PAN was fabricated by immersing the CB@PAN into the hydrophobic agent for 0.5 h and dried in an oven.

(3) Preparation of the CB-Ag@PAN

The CB-Ag@PAN was fabricated through an electroless Ag plating. The plating bath was prepared by mixing two solutions: firstly, 4 wt% glucose was dissolved into 10 mL of H$_2$O, noted as solution A. Then 4
wt% AgNO₃ and 10 wt% NaOH were first dissolved into 5 mL of H₂O, then dropwise added 500 µL of NH₄OH, noted as solution B. The CB@PAN was immersed in solution A, and solution B was dropwise added into solution A at 30°C. After being treated for 10 min, the CB-Ag@PAN was successfully prepared.

(4) Preparation of the CB-Ag-LiCl@PAN

A facile impregnation method was adopted to obtain CB-Ag-LiCl@PAN. The CB-Ag@PAN was immersed in the 30 wt% LiCl solution for 24 h and then dried in a vacuum oven at 90°C.

(5) Preparation of the San@PAN

The San@PAN was prepared as a sandwich structure by stacking the CB-PDMS@PAN (top layer), CB-Ag-LiCl@PAN (middle layer), and CB-PDMS@PAN (bottom layer). The diameter of the San@PAN is 5 cm, and the thickness is 2 mm.

Moisture absorption test

Before the absorption test, the nanofibrous membranes were placed in an oven at 100°C for 24 h to evaporate the moisture. The original mass of nanofibrous membranes was recorded, and the moisture absorption tests were applied in a constant humidity chamber at 20°C. The weight of the nanofibrous membranes was recorded by a balance. The water uptake rate of the nanofibrous membranes was calculated by the following Eq. (1):

\[ C_{abs} = \frac{\Delta m}{m_0} \]

Where \( C_{abs} \) represents the water uptake rate (g g⁻¹), \( \Delta m \) and \( m_0 \) represent the water absorption mass (g) and the weight of dried nanofibrous membranes, respectively. Each sample was tested 3 times, and the average value was recorded as the water uptake rate.

Water evaporation test

Before the test, the used nanofibrous membranes had reached absorption saturation. The saturated nanofibrous membranes were put in a culture dish at 25 °C and 50% RH, and a xenon lamp light source (CEL-S500) was installed over the petri-dish and performed the water evaporation test. The solar irradiation intensity was fixed at 1 kW m⁻². The mass change of the nanofibrous membranes was recorded every 5 min. Each sample was tested 3 times, and the average value was considered the water evaporation result.

Characterization

The surface morphology of the nanofibrous membranes was characterized by FE-SEM (S-4800). The detailed images of the nanofibrous membranes in moisture absorption and water evaporation processes were recorded by iPhone. XRD patterns were measured by an X-ray diffractometer (Bruker, Germany). The
surface chemical structure was tested through ATR-FTIR spectroscopy (Thermo Fisher Scientific, USA) and an energy dispersive spectrometer (EDS). The pore size and water transmission rate were measured by a Capillary flow porometer and computerized fabric moisture permeability meter. The wettability of nanofibrous membranes was characterized by optical contact angle meter system (Krüss DSA 100, Germany).

## Declarations

### ASSOCIATED CONTENT

Supporting Information: Supplementary Figures S1-S11.

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### Notes

The authors declare no competing financial interest.

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### References


Figures
Figure 1

(a) Selective permeability of phospholipid bilayer on the cell membrane. (b) The fabrication process of San-PAN. (c) Selective water harvesting and release of San-PAN. (d) Schematic illustration of the leakage process of samples with/without sandwich structure. (e) Schematic illustration of the water sorption/desorption process of the San-PAN.
Figure 2

SEM images of PAN (a), CB@PAN (b), CB-PDMS@PAN (c), and CB-Ag-LiCl@PAN (d). The contact angles of CB-PDMS@PAN (e), and CB-Ag-LiCl@PAN (f). (g) the pore size distribution of CB@PAN and CB-PDMS@PAN. (h) water transmission performance of PAN, CB@PAN, and CB-PDMS@PAN.
Figure 3

Water sorption mechanisms of San-PAN.
Figure 4

(a) Water uptake rate of CB-Ag-LiCl@San-PAN and CB-LiCl@San-PAN. (b) Cycling stability of water uptake rate of CB-Ag-LiCl@San-PAN at various humidities. (c) Water uptake rate and LiCl uptake rate of Ag@SanPAN and Ag@PAN. (d) Schematic of the water absorption behavior of LiCl particles. (e, f) Optical photographs reveal surface water absorption and leakage of Sin-PAN and San-PAN at 25°C and 90% RH. (g) Mechanism diagram of the water absorption behavior of San@PAN.
Figure 5

(a) The light absorption of the CB@PAN with different CB uptake rates. Solar spectral irradiance (orange shadow) weighted by standard AM 1.5 G solar spectrum. (b, c) Water uptake rate and mass change of the ORI@San-PAN and CB@San-PAN. (d) The surface temperature of the outer layer and inner layer of San-PAN. (e, f) Water uptake rate and mass change of the CB-Ag-LiCl@San-PAN and CB-LiCl@San-PAN. (g, h) Infrared radiation thermal images reveal the surface temperature distribution of the outer and inner layers under one-sun illumination. (i) Schematic displaying of the photothermal properties of the San@PAN.
Figure 6

AWH under practical solar irradiation. (a-c) Optical images of the surface of the water harvesting device collected water and solar radiation intensity. (d, e) Practical water uptake rate, water evaporation rate, corresponding RH, and temperature. (f) The wearability of San-PAN. (g) The potential application models of the wearable San-PAN for outdoor water supply.
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