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Hollow Spherical SiO_2 Micro-Container Encapsulation of LiCl for High-Performance Simultaneous Heat Reallocation and Seawater Desalination

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Structure characterization

The surface structure of sorbents was characterized by FE-SEM (Teneo VS, FEI) and its Si, Cl content was detected by the equipped energy-dispersive X-ray spectroscopy. XRD patterns were collected on a D2 Phaser Bruker X-ray diffractometer with Cu Kα radiation. During the evaluation, certain amount sorbent was loaded on the non-reflective substrate and covered by non-reflective polymer layer to isolate the water molecule in surrounding air during characterization. Nitrogen sorption isotherms were measured on a TriStar II 3020 (Micromeritics Instrument Corporation). Before the measurement, samples were pre-dried under N_2 atmosphere at 100 °C for 12 hours.

Water sorption performance evaluation

Water vapor sorption kinetics were measured by a Jupiter simultaneous thermal analyzer system (STA 449F3, Netzsch) equipped with a modular humidity generator (MHG 32, Proumid). For a typical evaluation, 5 mg of the sorbent was placed on a microbalance under a specific relative humidity (RH) (e.g., 20%, 50% or 80%) at 25 °C. The change of the sorbent weight was recorded and each measurement lasted for 700 min.

Water sorption and desorption cycling experiments were performed by the same system (STA 449F3, Netzsch). The cycle was composed of a stabilization step at 25 °C, a sorption step for 180 min under 50% RH condition, followed by a desorption step at 70 °C and 20% RH for 180 min. This sorption-desorption cycle was repeated for 10 times.

Water vapor sorption isotherms were evaluated on a water sorption analyzer (IGAsorp, Hiden Isochema). For a typical measurement, 20 mg sorbents were loaded into the microbalance inside the analyzer. The sample was first dried at RH 0% until the sample's weight did not change anymore. Thereafter, the instrument can regulate the RH automatically from 5% to 85% with an interval of 5%. At each RH step, the equilibrium sorption capacity was determined by recoding the weight change in real time till the weight change rate was approaching zero. The maximum equilibration time was set as 250 min to ensure the full saturation.

Calculation of sorption enthalpy

The enthalpy of sorption was calculated from the isotherms measured at two different temperatures, according to the Clausius-Clapeyron equation.[1,2]

$$\Delta H_{ads} = \frac{T_1 T_2}{T_2 - T_1} RLn\frac{P_2}{P_1} \qquad \text{Equation 1}$$

Where ΔH_{ads} (J/mol) is the sorption enthalpy of water on the sorbent, R is the ideal gas constant, which is 8.314 J/mol·K. T_1 (K) and T_2 (K) are the temperatures at which the isotherms were measured, and P_1 (kPa), P_2 (kPa) are the corresponding vapor pressures at a specific sorption amount.

Calculation of characteristic curves

In order to extrapolate the sorption isotherms at any given temperatures, characteristic curve, which is based on Polanyi sorption theory, is applied. It ascribes the water uptake value to one single parameter (i.e., adsorption potential), rather than two parameters, namely, pressure and temperature.[3] The conversion process can be described in Equation 2:

$$A = RTLn(\frac{P_0(T)}{P}) \qquad \text{Equation 2}$$

Where A (J/mol) is the adsorption potential, which is the negative of Gibbs free energy of adsorption, R is the ideal gas constant, T (K) is the adsorption temperature, P_0(T) (kPa) is the saturation vapor pressure at adsorption temperature, and P is the vapor pressure at each water uptake value. From the isotherms measured in this work, the adsorption potential was calculated at each water uptake point. Assuming that the adsorption potential is a constant for any specific water uptake condition, i.e. the adsorption potential is independent of temperature, and then the isotherms, water uptake vs. water vapor pressure, can be thereafter calculated for any a given temperature (Fig. S23).

Calculation of heat transfer per cycle as a function of temperature lift

For heat pump application, temperature lift means the temperature difference between sorbents (or condenser) and evaporator. Here, we set the condenser temperature constant at 30 °C. On the other hand, the evaporator temperature is not constant and varies depending on vapor sorption stages by the sorbent. The desorption temperature, or adsorbent regeneration temperature, was set at 100 °C which is the highest temperature of common solar collector. The minimal (W_{min}) and maximal (W_{max}) water vapor adsorption capacity of the sorbent is calculated according to the derived isotherms. The saturation capacity, W_{max} was calculated at the sorbent temperature of 30 °C for various water vapor pressure, which is determined by the evaporator temperature, from 0 °C (30 °C lift) to 30 °C (0 °C lift). W_{min} is calculated for the sorbent temperature at 100 °C with desorption water vapor pressure, which is determined by the temperature of the condenser. The difference of $\Delta W = W_{max} - W_{min}$ means how many water is removed from the source water to the sorbent in one absorption cycle. Then the heat transfer from water can be calculated following the Equation 3 (Fig. S17):[4]

$$HT = \frac{Q_{evp}}{m} = \frac{\Delta H_{evp}(T_{evp})\Delta W}{m} \quad \text{Equation 3}$$

Where HT (kWh/kg) is the heat transfer per cycle, Q_{evp} (kJ) is the heat transferred by evaporation per cycle, ΔH_{evp} (kJ/kg) is the water evaporation enthalpy at the evaporator temperature, ΔW (kg/kg) is the working capacity of sorbent at certain condition, and m (kg) is the weight of sorbents.

Calculation of the coefficient of performance (COP)

Briefly, COP for cooling (COP_C) and COP for heating (COP_H) is defined by:[4]

$$COP_C = \frac{Q_{evp}}{Q_{regen}} \quad \text{Equation 4}$$

$$COP_H = \frac{Q_{sorption} + Q_{cond}}{Q_{regen}} \quad \text{Equation 5}$$

Q_{evp} (kJ) is the energy taken by evaporation, defined as:[4]

$$Q_{evp} = \Delta H_{evp}(T_{evp})\Delta W \quad \text{Equation 6}$$

ΔH_{evp} (kJ/kg) is the water evaporation enthalpy at the evaporator temperature and ΔW (kg/kg) is the working capacity of sorbent.

Q_{sorption} is the energy released during adsorption, which can be calculated as:[4]

$$Q_{sorption} = \frac{1}{M_w}\int_{m_{min}}^{m_{max}} \Delta H_{ads}(m)dW \quad \text{Equation 7}$$

Here, ΔH_{ads} (kJ/mol) is the enthalpy of adsorption. And M_{w} is the molar mass of working fluid (18 g/mol for water).

Q_{cond} is the energy released during adsorption which can be calculated as:[4]

$$Q_{cond} = \Delta H_{cond}(T_{cond})\Delta W \quad \text{Equation 8}$$

ΔH_{cond} (kJ/kg) is the condensation enthalpy at the condenser temperature and ΔW (kg/kg) is the working capacity of sorbent.

Q_{regen} (kJ) is the energy required for sorbent regeneration, defined as:[4]

$$Q_{regen} = \int_{T_{cond}}^{T_{des}} C_p^{sorbent}(T)dT_{eap} + \int_{T_{cond}}^{T_{des}} \frac{m_{max} + m_{min}}{2} C_p^{wf}(T) - Q_{sorption} \quad \text{Equation 9}$$

$C_{\mathrm{p}}^{\mathrm{sorbent}}$ (J/kg/K) and $C_{\mathrm{p}}^{\mathrm{wf}}$ (J/kg/K) is the heat capacity of sorbent and working fluid. In this study, the working fluid is water. m_{max} (kg/kg) and m_{min} (kg/kg) is the working capacity of the sorbent at adsorption and desorption condition.

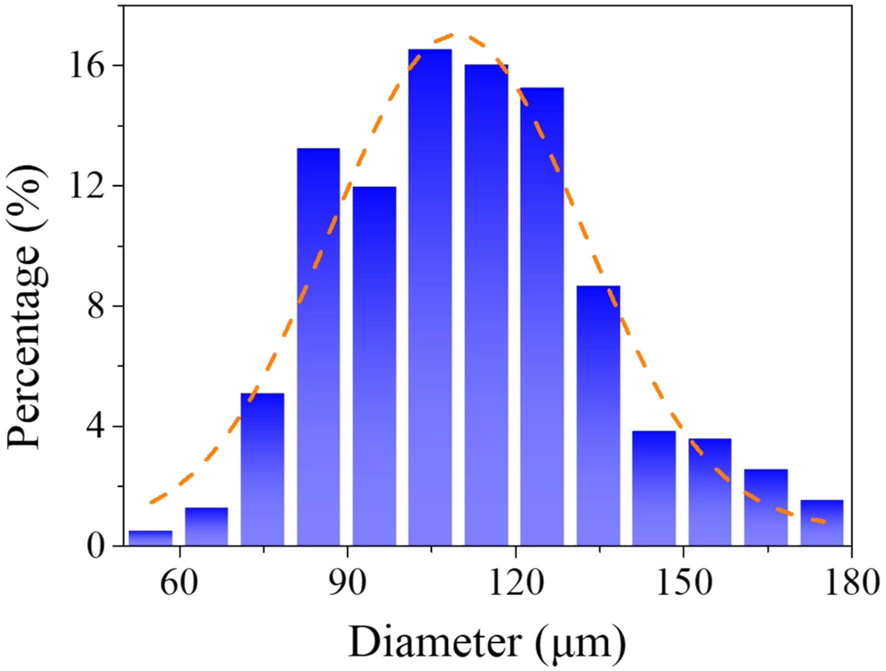

Figure S1. Histogram of the diameter distribution of the fabricated HS.

Size statistic is based on the measurements obtained from more than 500 randomly acquired samples. Statistic result shows the size of HS is range between 60–180 μm, with a mean particle size of 100 μm.

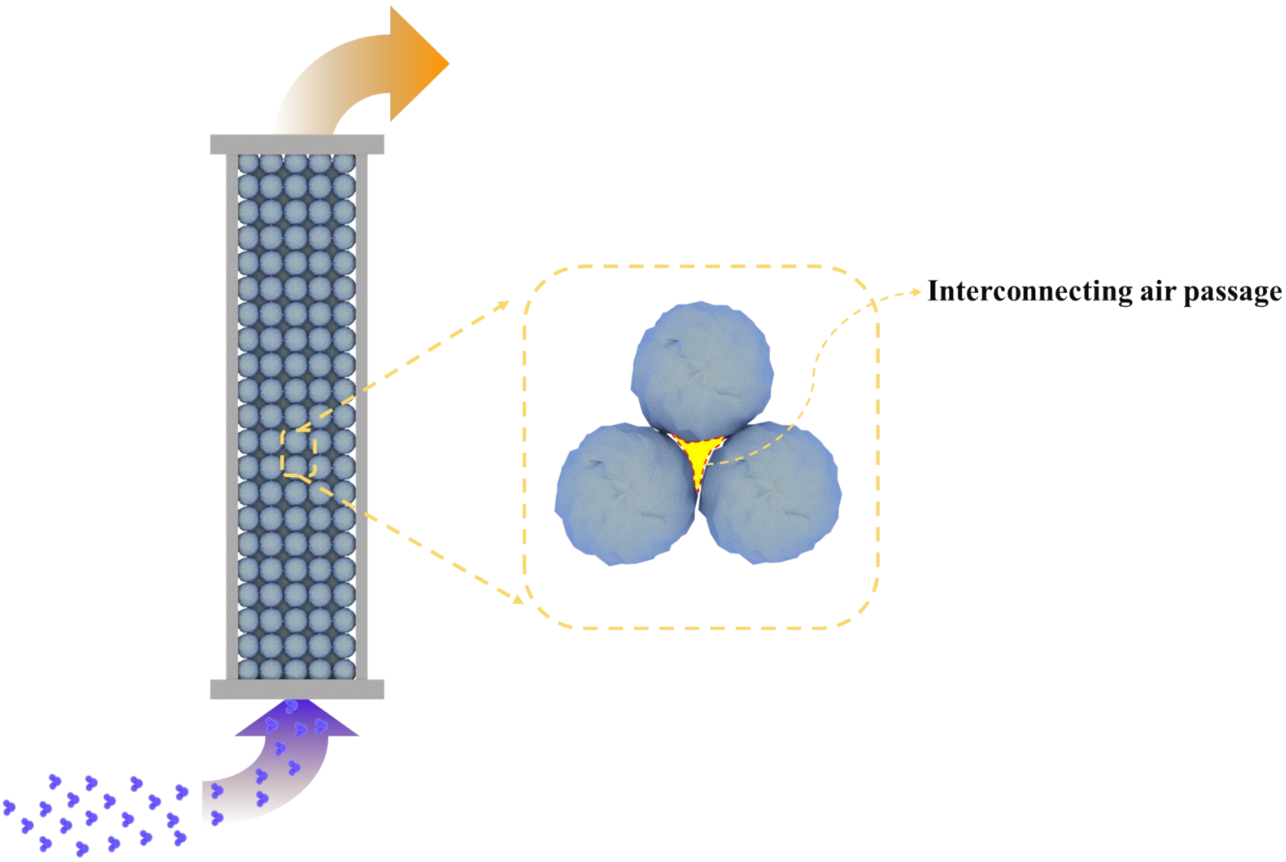

Figure S2. Schematic diagram of sorbents filled adsorption bed.

As presented in the diagram, due to the micron size of particles, there are sufficient and interconnecting channels for efficient air transport inside the adsorption bed.

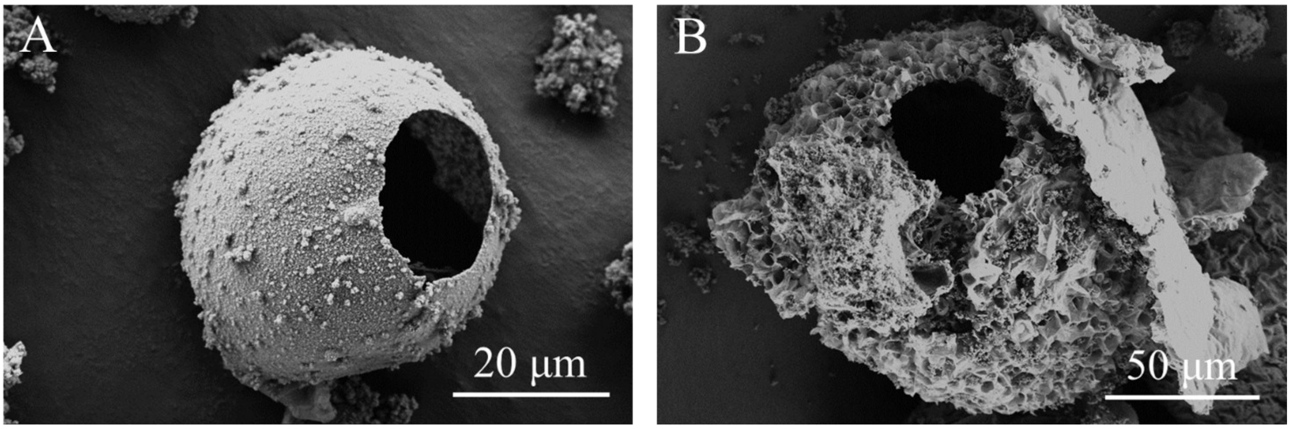

Figure S3. SEM images of broken HS.

Broken particles are selected from the fabricated HS and the images clearly reveal the hollow structure and their thin shell.

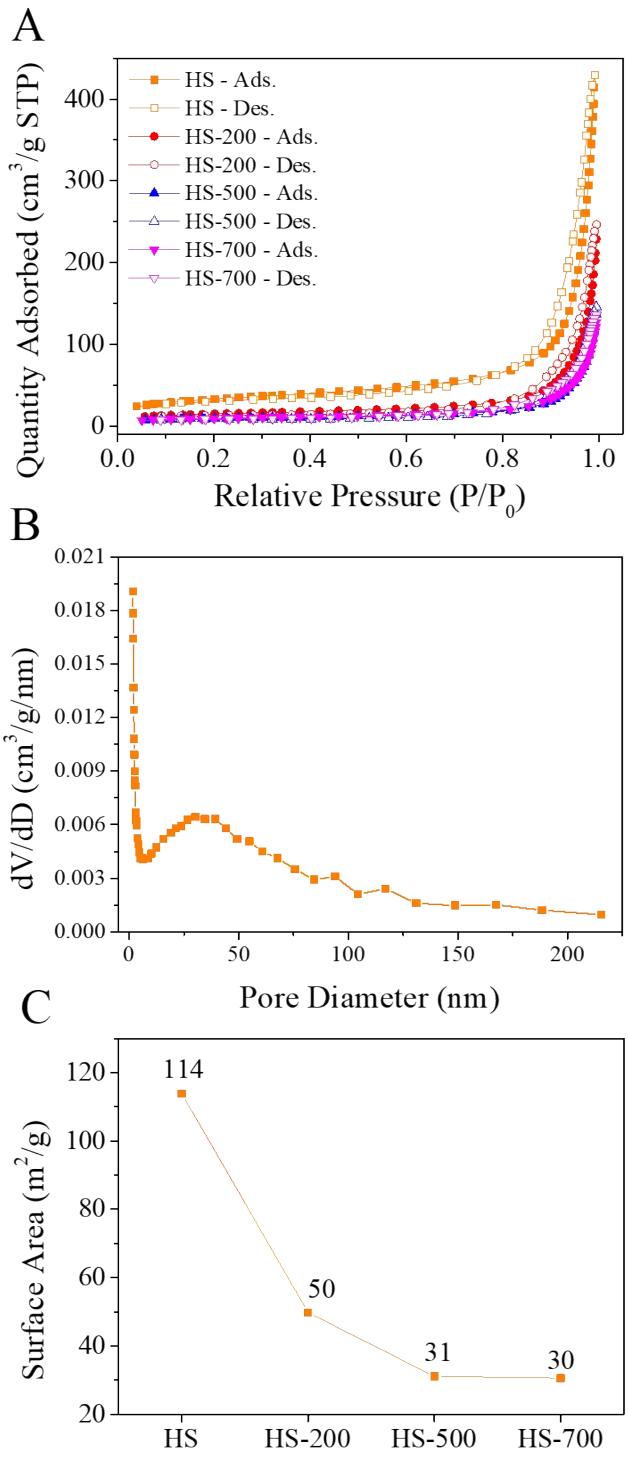

Figure S4. Surface area and pore structure of sorbents. (A) N_2 adsorption-desorption isotherms of HS and LiCl@HS, **(B)** Pore size distribution curves of HS, **(C)** Surface areas of HS and LiCl@HS. The result shows that HS possess a mean pore size distribution at 30 nm. And the specific surface area of HS, HS-200, HS-500, and HS-700 is 114, 50, 31 and 30 m^2/g respectively.

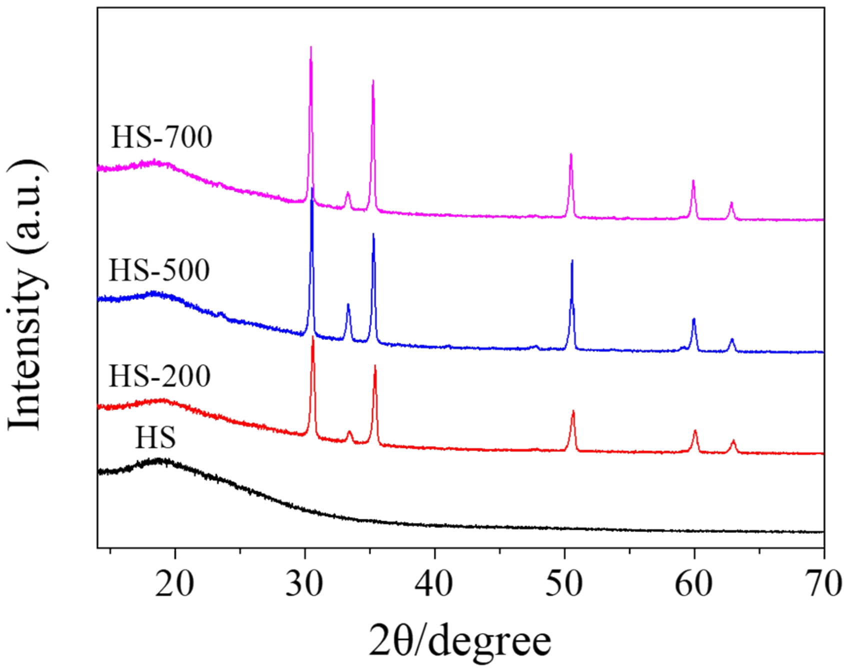

Figure S5. XRD patterns of HS and LiCl@HS.

HS shows one weak and broad peak. While all LiCl@HS show additional sharp peaks originated from LiCl crystal.

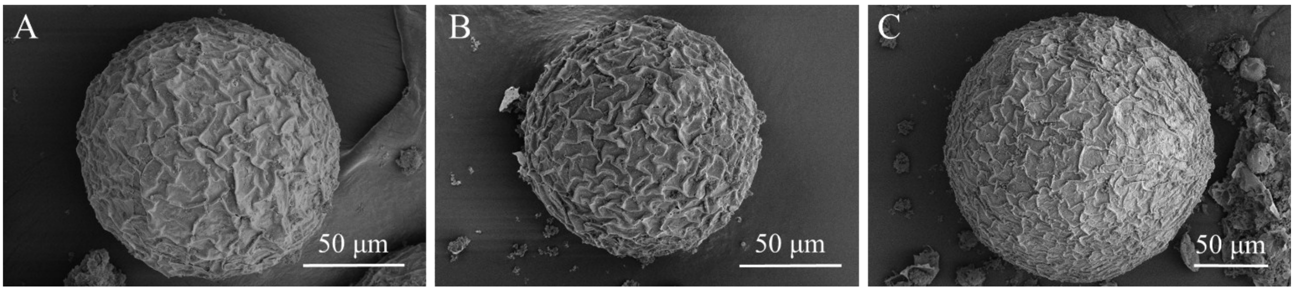

Figure S6. SEM images of the surface morphology of HS. (A) HS-200, **(B)** HS-500, **(C)** HS-700.

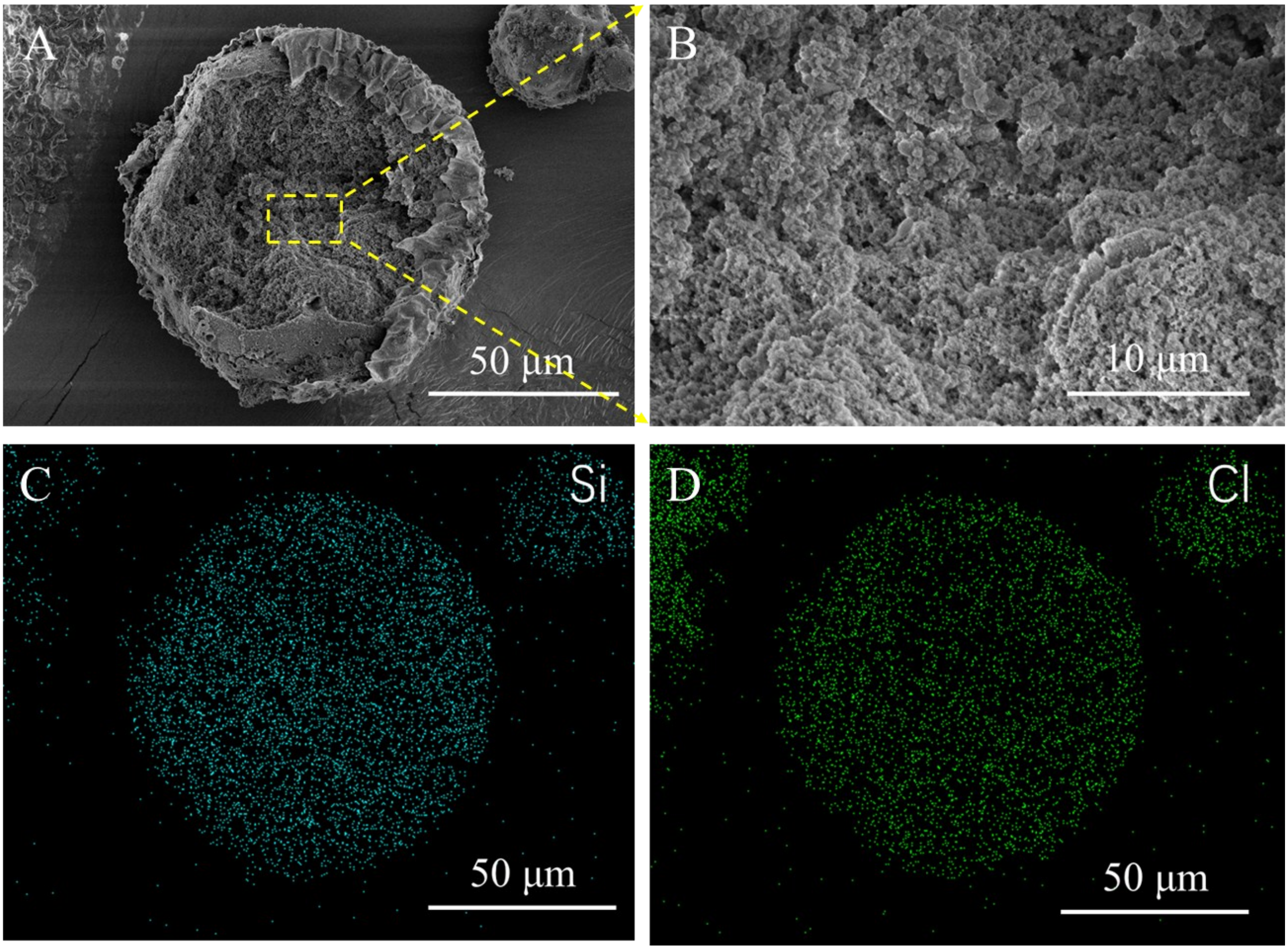

Figure S7. Structure characterization of broken HS-500. (A) SEM image of broken HS-500, **(B)** Magnified image of the circled area in (A), **(C)** Si signal of EDS characterization, **(D)** Cl signal of EDS characterization.

Broken HS-500 reveals the crystal inside the hollow sphere while EDS show strong Cl signal.

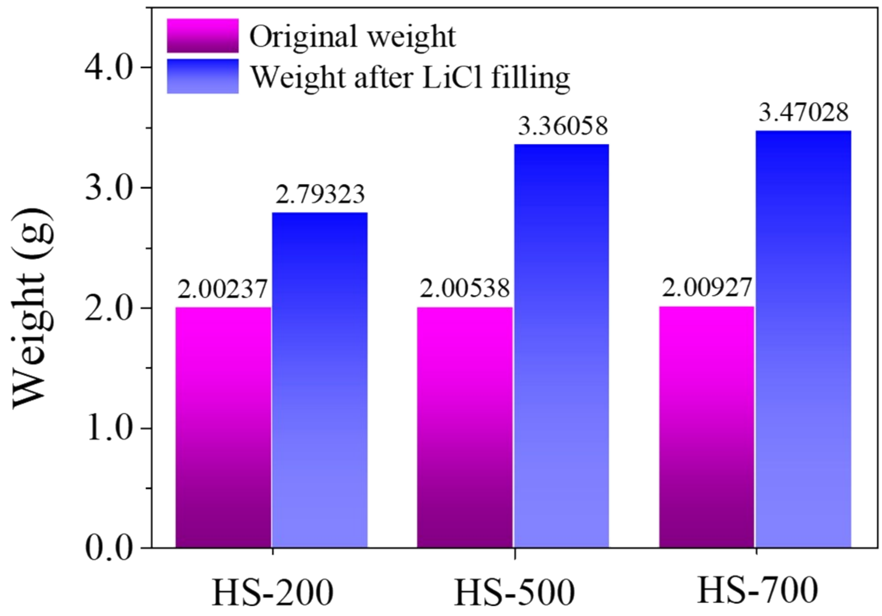

Figure S8. Weight change of HS after LiCl filling.

As revealed, LiCl content in LiCl@HS is determined to be 39.5% for HS-200, 67.6% for HS-500 and 72.7% for HS-700.

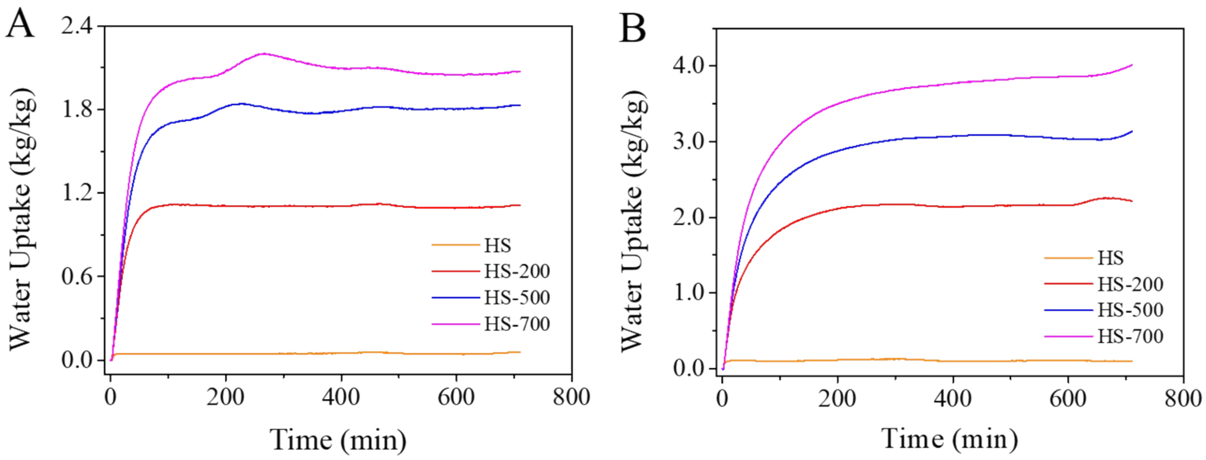

Figure S9. Adsorption kinetics of sorbents at different RH (A) 50% RH, **(B)** 80% RH.

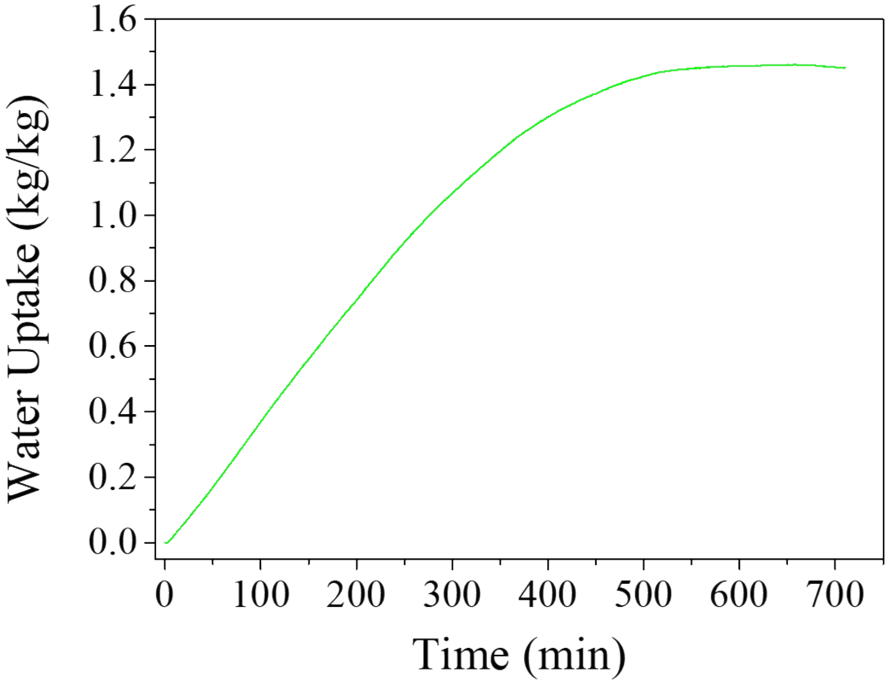

Figure S10. Adsorption kinetics of LiCl at 25 °C with 20% RH.

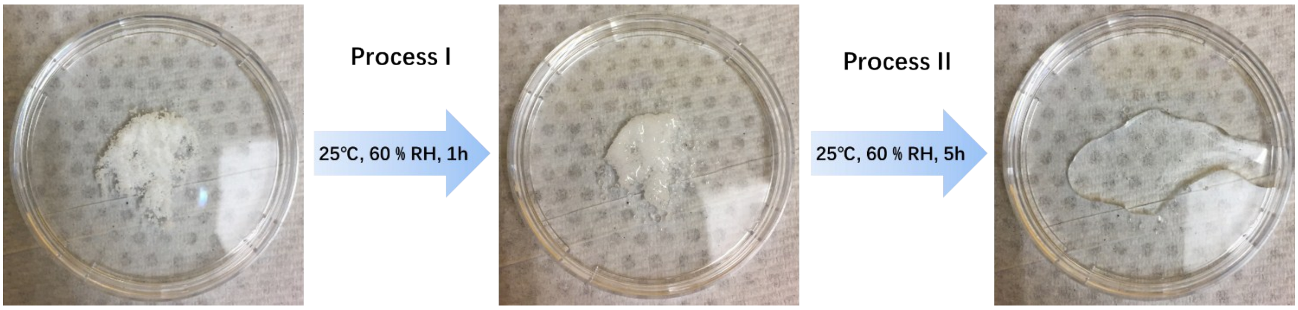

Figure S11. Visual observation of morphology change of LiCl salt under the condition of 60% RH at 25 °C.

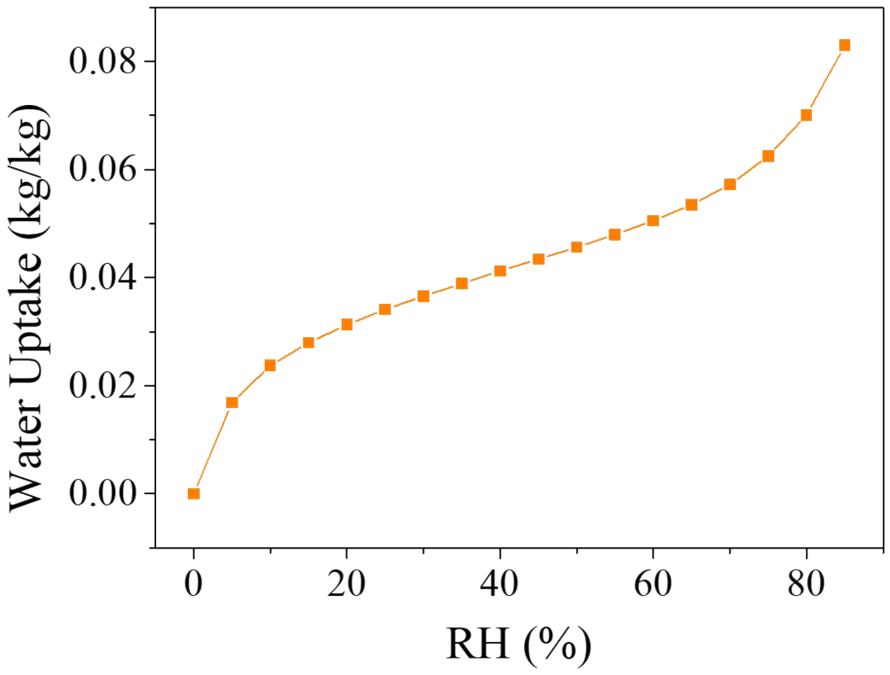

Figure S12. Water adsorption isotherm of HS at 25 °C**.**

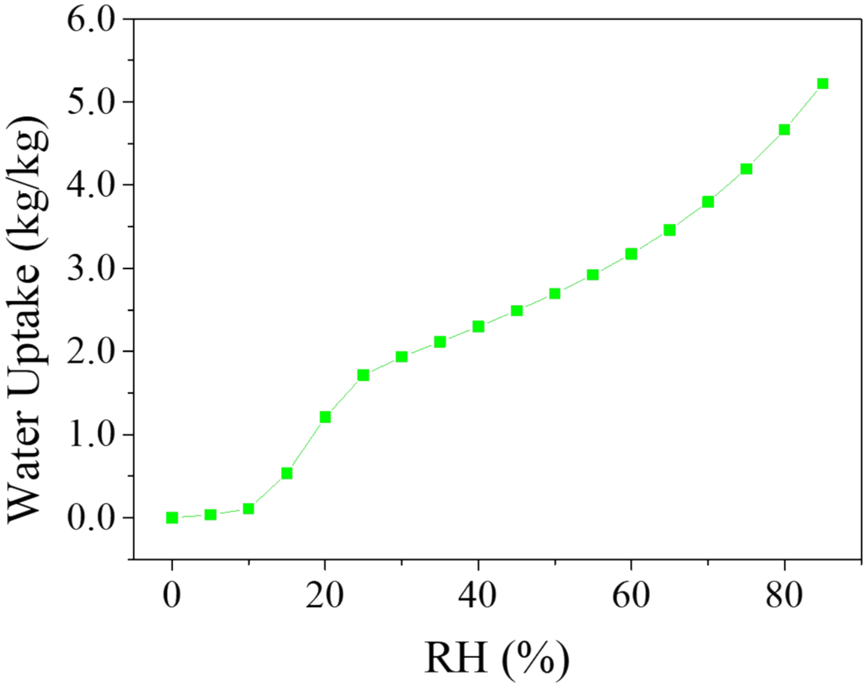

Figure S13. Water adsorption isotherm of LiCl at 25 °C.

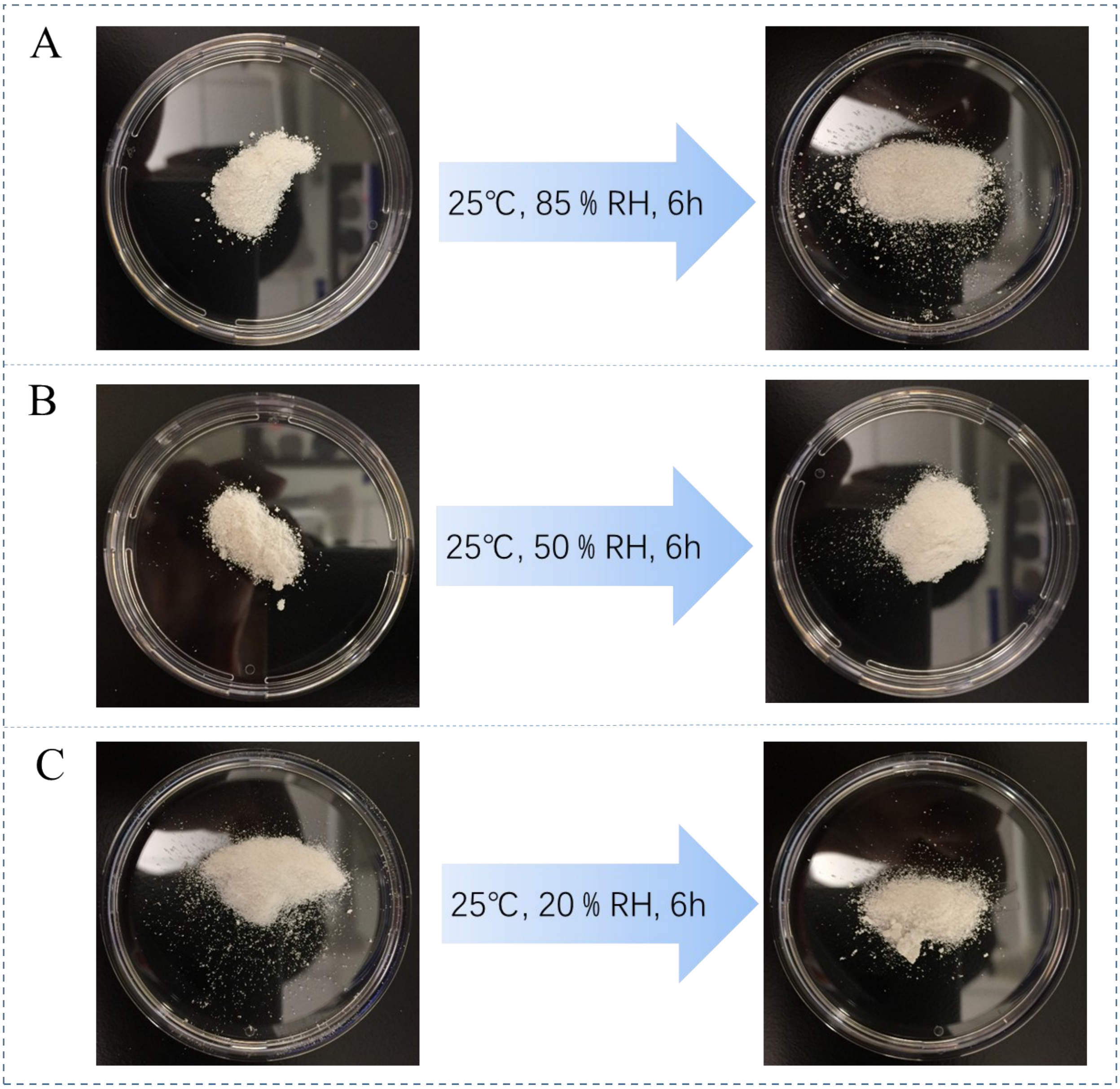

Figure S14. Visual observation of morphology change of LiCl@HS under certain condition. (A) HS-200 after 6 h at the condition of 25 °C, 85% RH, **(B)** HS-500 after 6 h, at the condition of 25 °C, 50% RH, **(C)** HS-700 after 6 h, at the condition of 25 °C, 20% RH.

At the condition of 85% RH, HS-200 still maintained morphology as powder form particles, so was HS-500 under 50% RH and HS-700 under 20% RH. Unchanged surface morphology indicates that adsorbed water was all stored in the hollow void with no leakage.

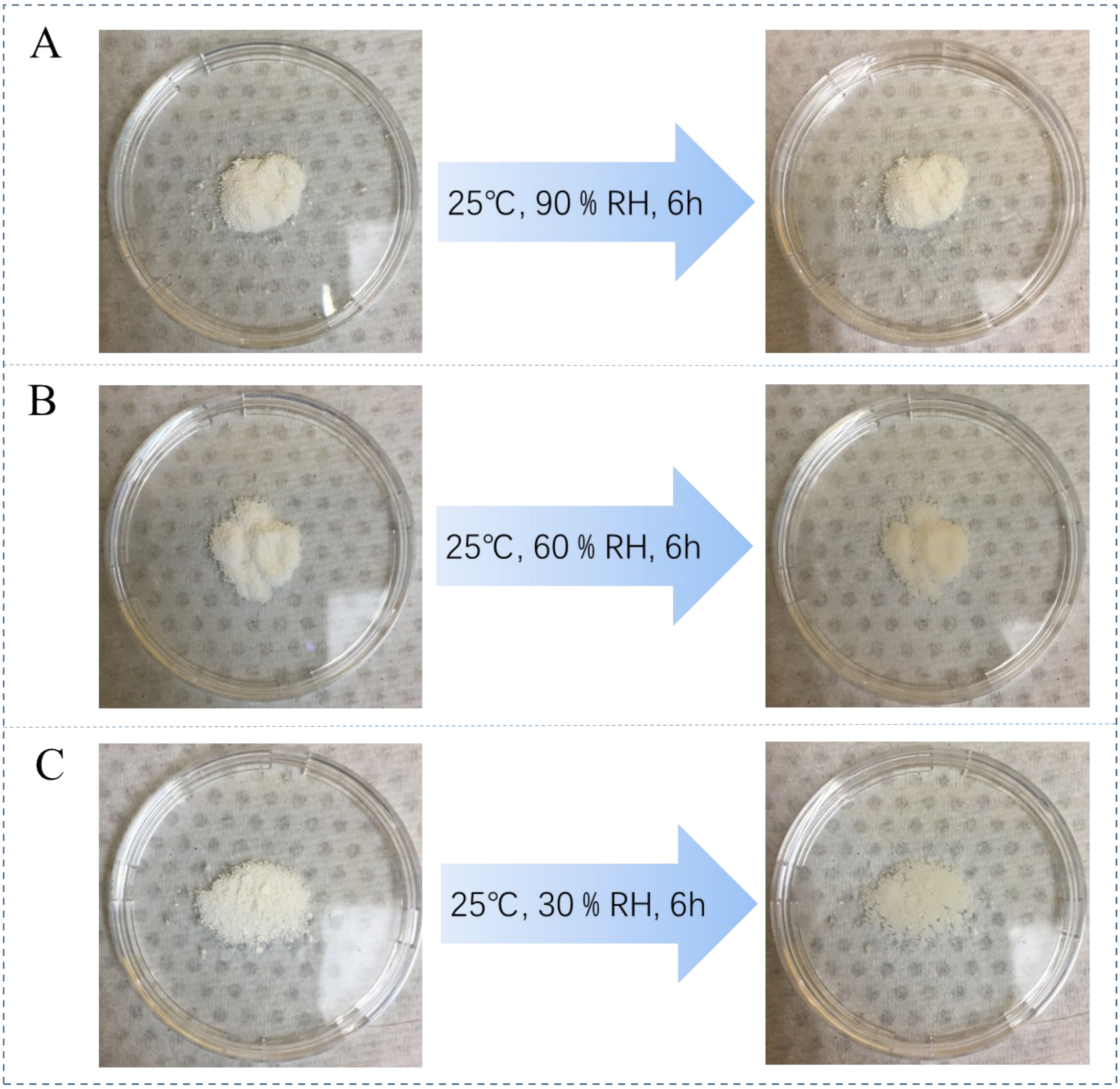

Figure S15. Visual observation of morphology change of LiCl@HS under certain condition. (A) HS-200 after 6 h, at condition of 25 °C, 90% RH, **(B)** HS-500 after 6 h, at condition of 25 °C, 60% RH, **(C)** HS-700 after 6 h, at condition of 25 °C, 30% RH.

Comparing with the initial one, HS-200, HS-500 and HS-700 became wet with particles sticking together, indicating that sorbents were saturated and the sorbed water overflew outside the sorbent shells.

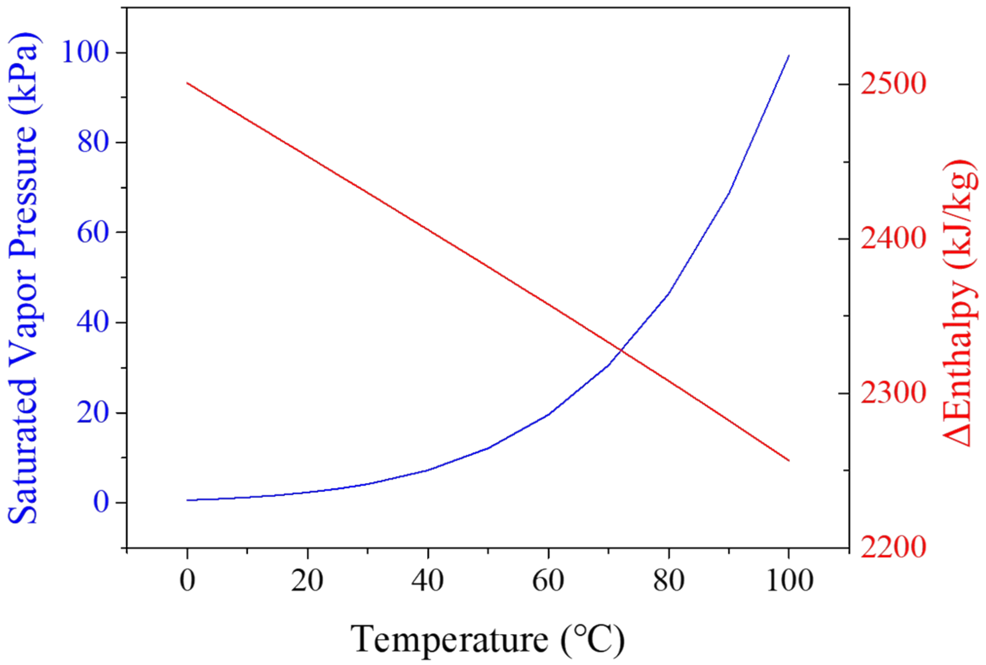

Figure S16. Saturated vapor pressure and evaporation enthalpy of seawater (Salinity 3.5%) as a function of temperature. (Dates from Ref. 1)[1]

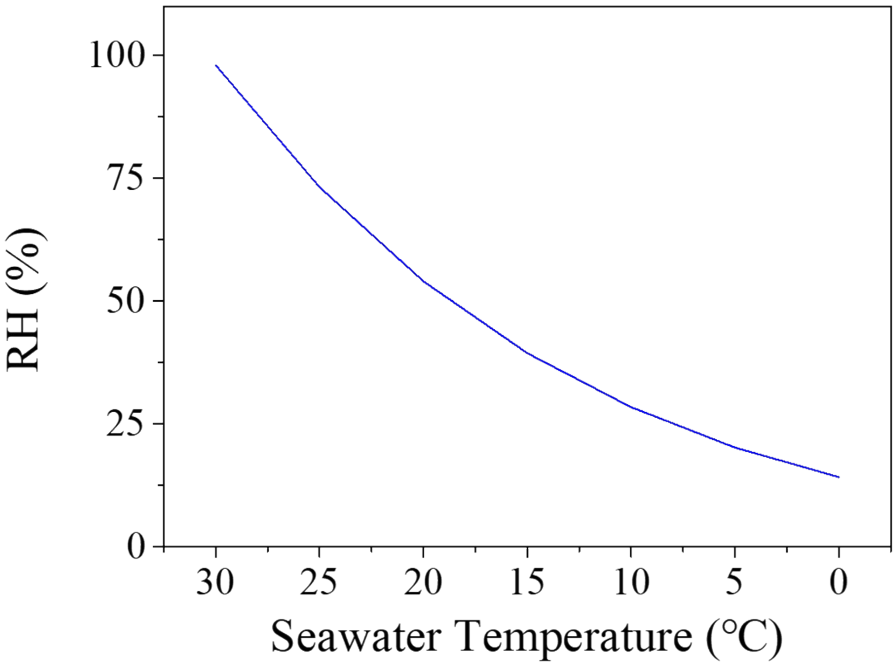

Figure S17. RH variation around the adsorbents at 30 °C, according to the temperature of seawater.

When the working temperature of sorbents maintained at 30 °C, the RH around sorbents is depend on the temperature of the seawater source. Saturated vapor pressure of seawater (3.5 % salinity) presented in Fig. S9. RH around sorbents is calculated by seawater vapor pressure at working temperature divided by the saturated water vapor pressure at 30 °C. As LiCl@HS with different LiCl content suitable for different RH condition, HS-200 is suitable for temperature lift ≤ 12 °C, HS-500 is suitable for temperature lift between 12 °C–25 °C and HS-700 is suitable for temperature lift ≥ 25 °C.

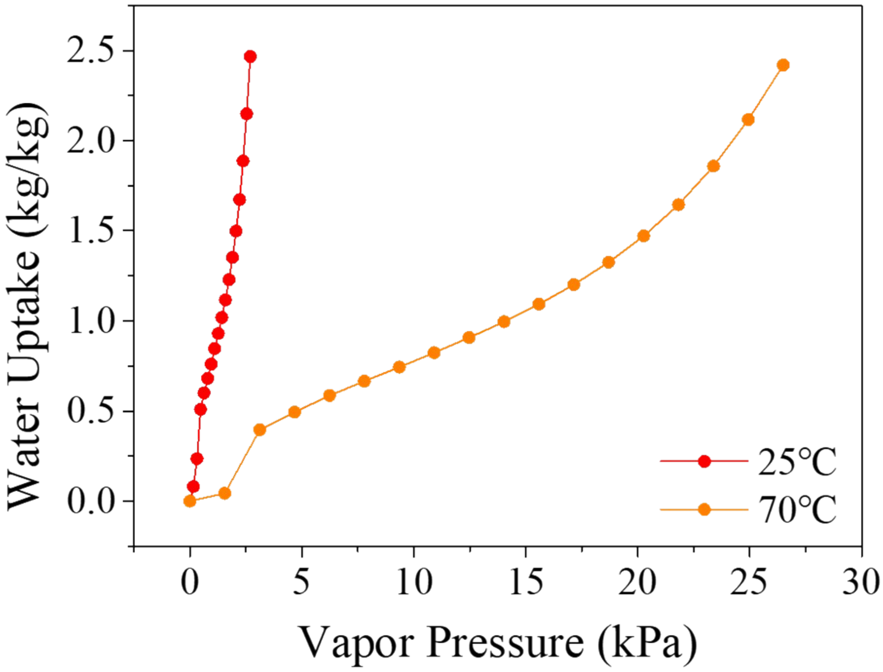

Figure S18. Water adsorption isotherms of HS-500 at 25 °C and 70 °C.

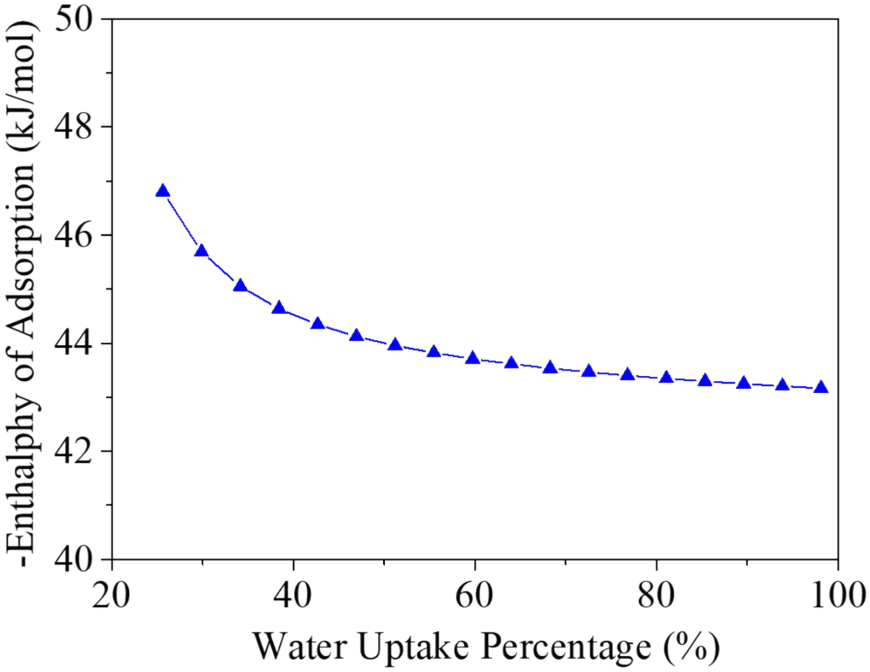

Figure S19. Adsorption enthalpy for water on HS-500.

The calculation is according to the Clausius-Clapeyron equation. The average enthalpy of adsorption is 44 kJ/mol which is equal to the evaporation enthalpy of water at 30 °C (2430 kJ/kg equal to 44 kJ/mol) (Fig. S16).

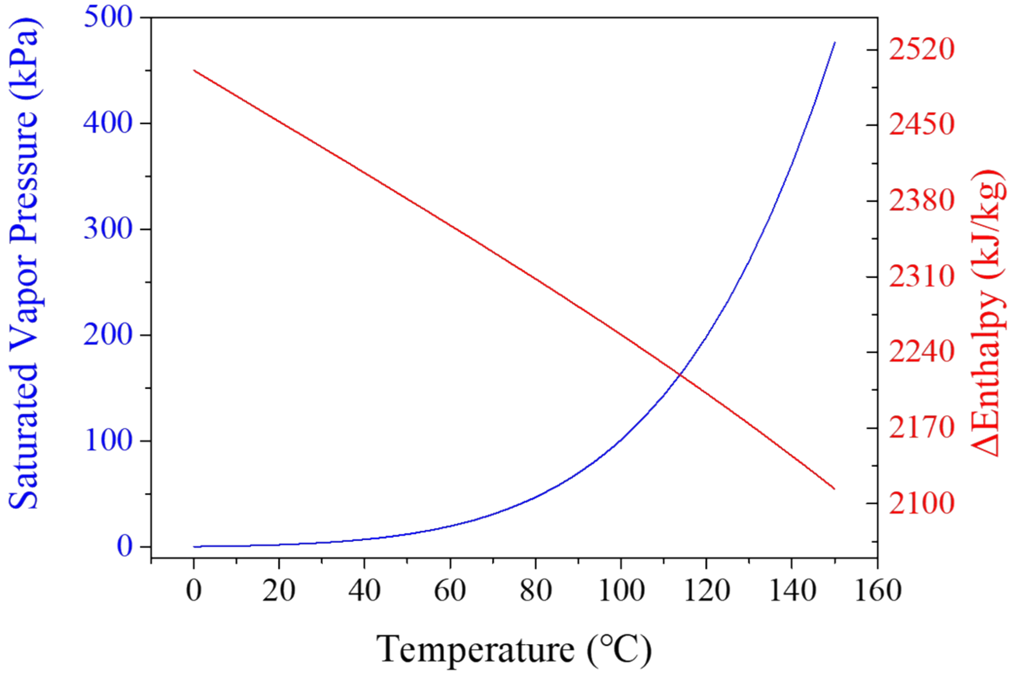

Figure S20. Water saturated vapor pressure and evaporation enthalpy as a function of temperature. (Dates from Ref. 1 and 5)[1,5]

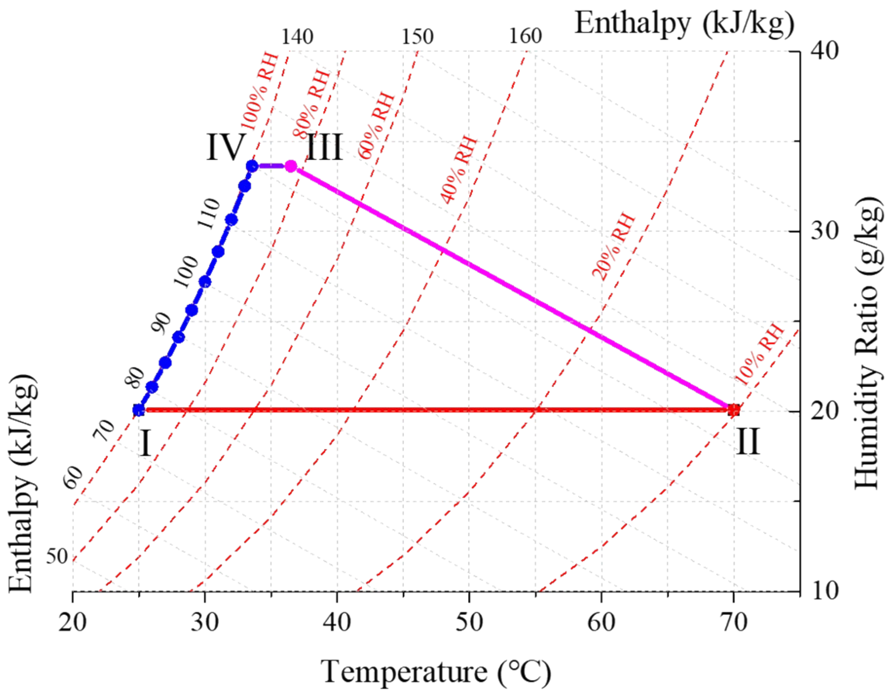

Figure S21. Psychrometric chart for desorption phase.

Desorption process can be explained by the psychometric chart.[6] The point I indicates the condition of air just exiting condenser. Once passing through the solar collector, the air is heated up from 25 °C to 70 °C. Desorption takes place in the stage of II–III. Once the hot air flow contacts with the saturated sorbent, sorbed water begin to release and the humidity in air increase. During this process the enthalpy keeps invariant. After the humidified air enters into the condenser, air's temperature decreases (III–IV). Vapor become condensed to water, once it reaches its dew point. The air temperature continually decreases, companied with more condensed water production, until it's temperature equal to the condenser (IV–I).

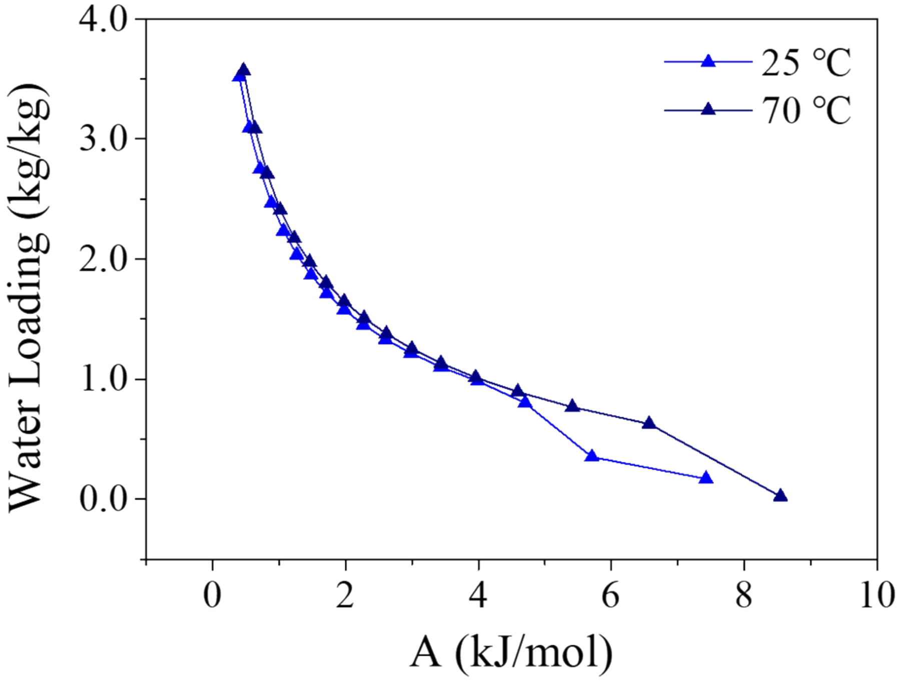

Figure S22. Characteristic curves for water vapor adsorption in HS-500.

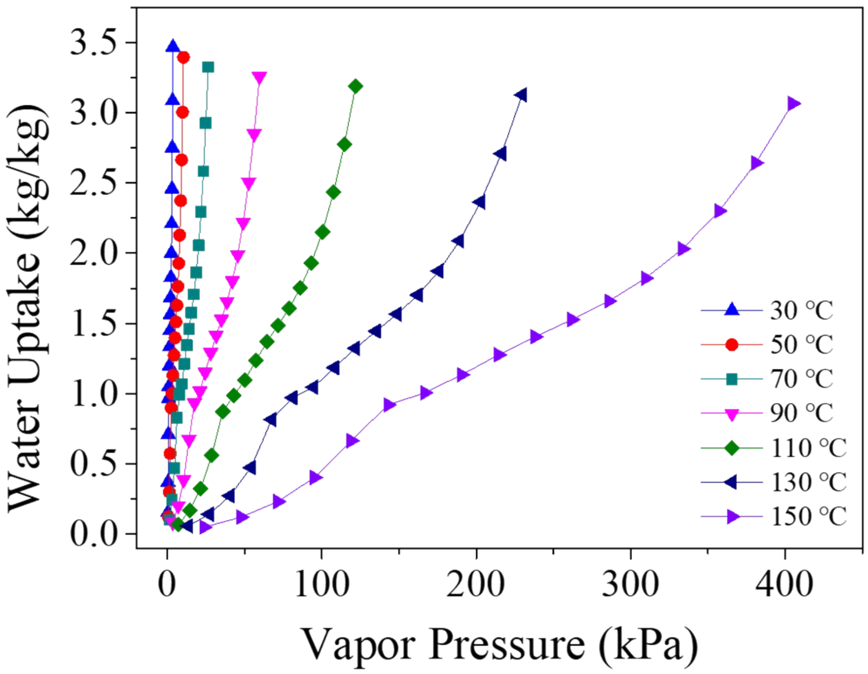

Figure S23. Extrapolated adsorption isotherms of HS-500 at other working temperatures.

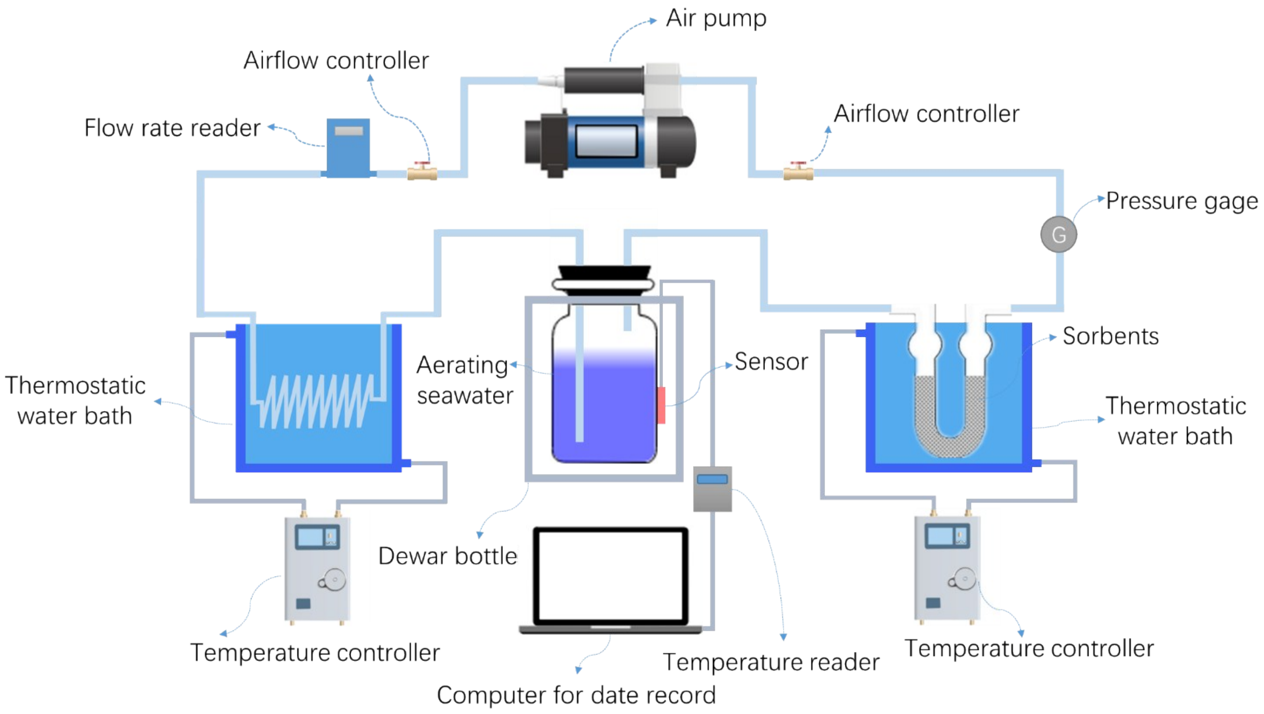

Figure S24. Laboratory devise for cooling evaluation.

The continuous airflow was driven by an air pump. The flow rate inside the piping system was regulated by the airflow controller and monitored by a mass flowmeter. A pressure gage was used to monitor the pressure. In our experiment, airflow was set at 500 ml/min and the pressure was kept at atmospheric pressure. The temperature of the water bath was set at 30 °C to maintain the inlet air temperature and sorbents temperature at simulated ambient condition (30 °C). Temperature variation of seawater in aeration bottle was measured by a thermocouple and recorded by a computer. With the adsorption going on, seawater could be gradually cooled from 30 °C to 8 °C.

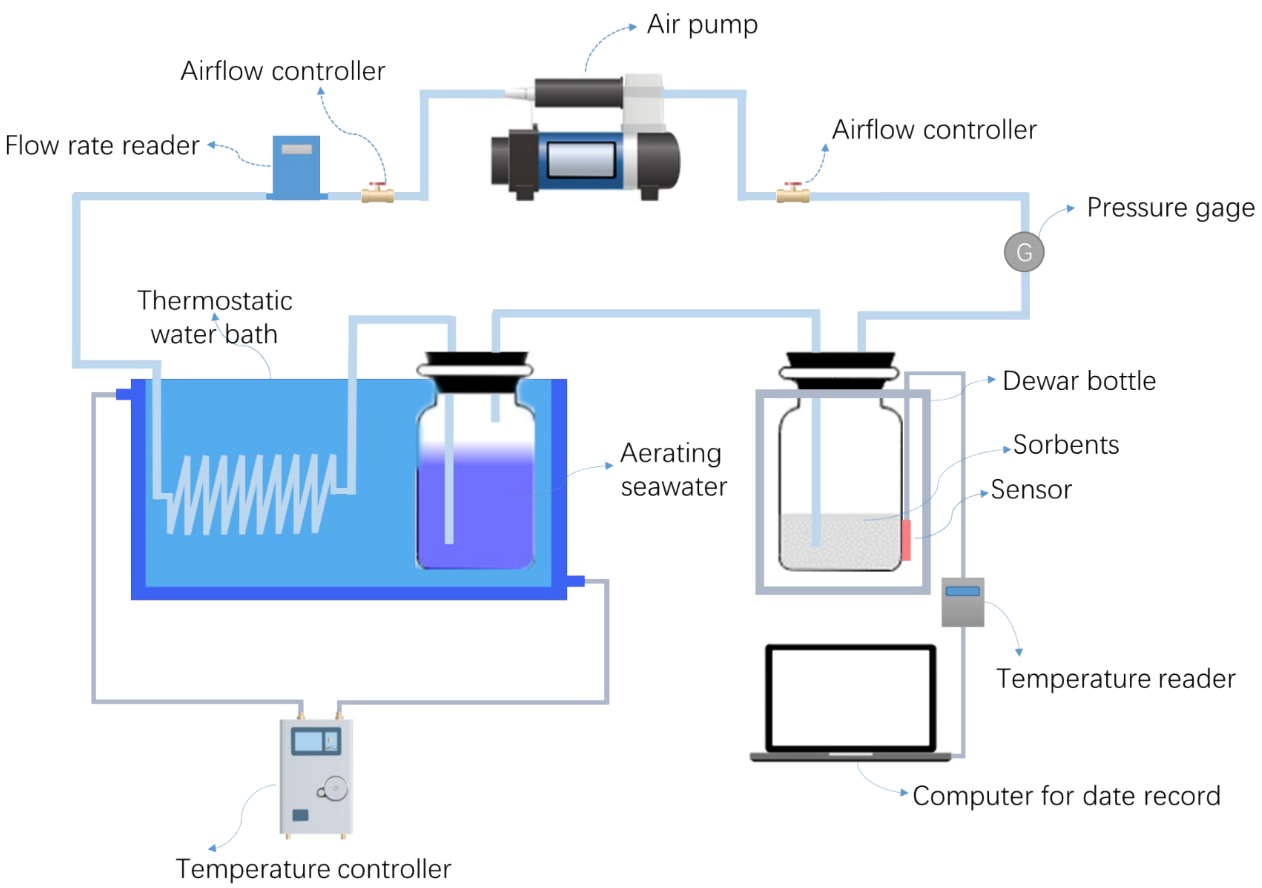

Figure S25. Laboratory devise for heating evaluation.

In this experiment, the temperature of the water bath was set at 10 °C to simulate the cold weather. Aerating seawater had 2.29 kPa as its water partial pressure. With the adsorption going on, adsorption heat was gradually released and the sorbent temperature could be raised from 10 °C to 32 °C.

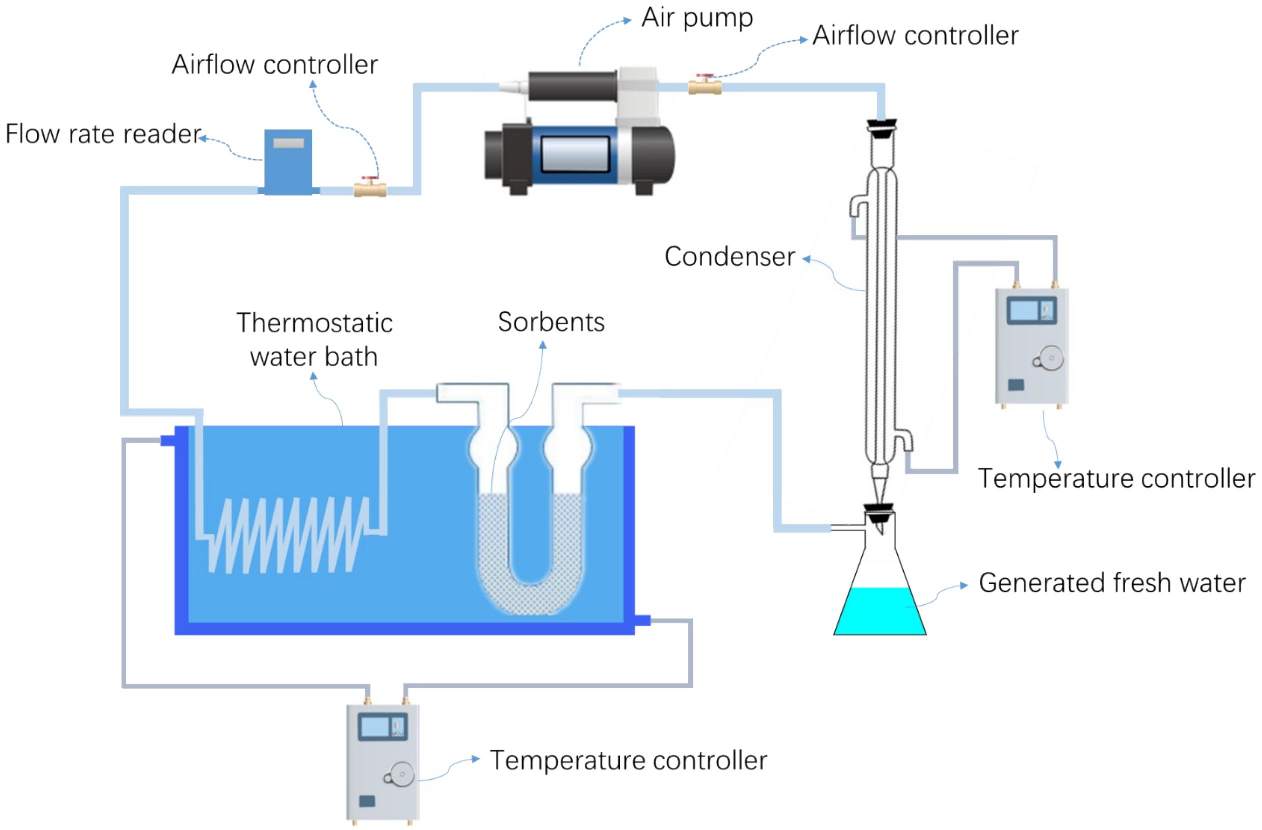

Figure S26. Laboratory setup for water generation assessment.

In this experiment, the temperature of the water bath was controlled at 80 °C to simulate the desorption temperature achievable by a solar collector. As the room temperature in the laboratory was around 25 °C, so the condenser was also maintained at 20 °C to avoid the water condensing in the back line.

Figure S27. Location of the seawater collection point (22.3° N, 39.1° E).

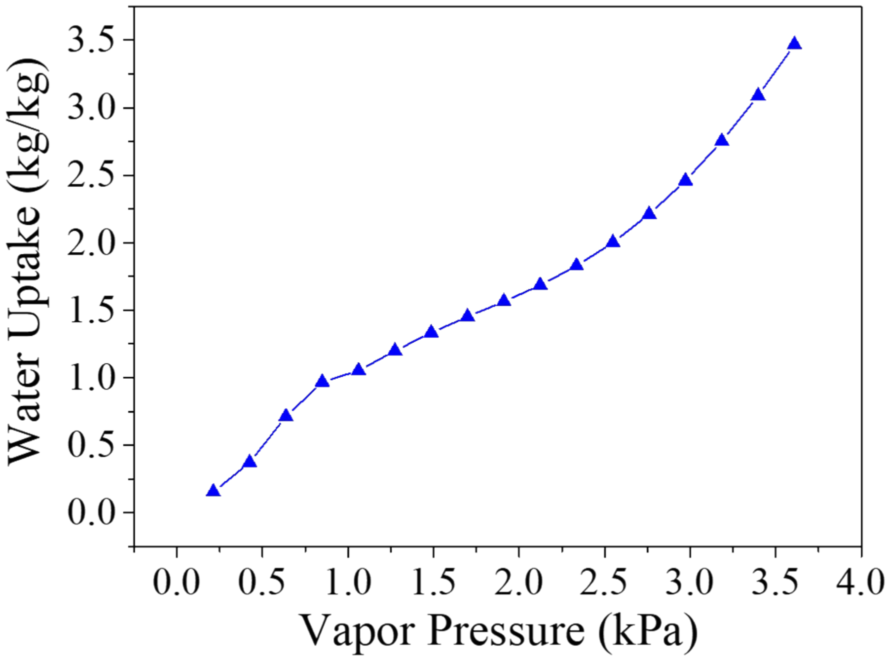

Figure S28. Adsorption capacity of HS-500 at 30 °C as a function of vapor pressure.

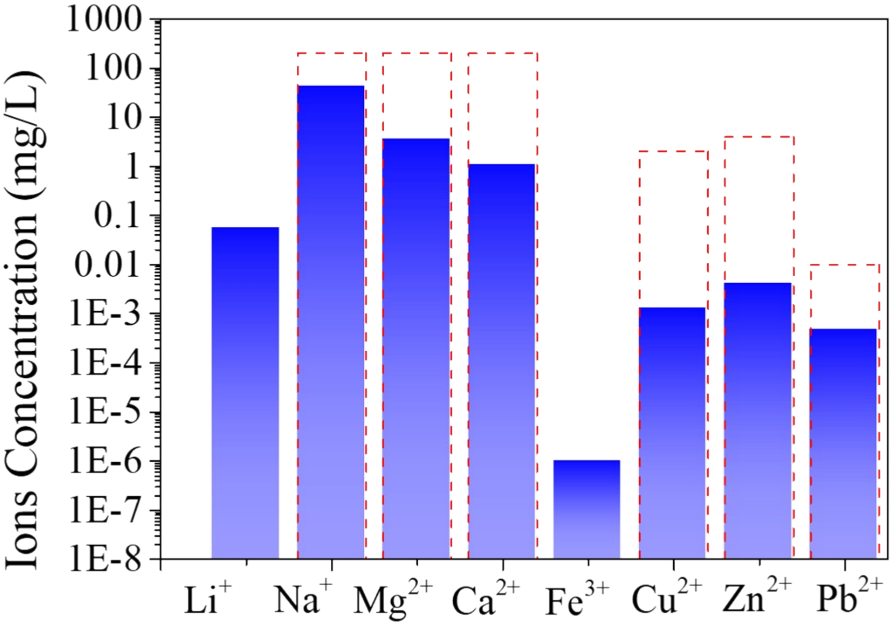

Figure S29. Ions' concentration in the produced water (i.e., condensed water) determined by ICP-MS.

Solid blue columns indicate the concentration of ions in the produced water while the dash red line bordered blank columns are the drinking water standard from WHO. Note: among these ions, the standards of Li^+ and Fe^{3+} are not given by WHO.

■ *References for SI*

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