Improving atmospheric water production yield: enabling multiple water harvesting cycles with nano sorbent

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Abstract

Clean water shortage has long been a challenge in remote and landlocked communities especially for the impoverished. Atmospheric water is now considered as an unconventional but accessible fresh water source and sorption-based atmospheric water generator (AWG) has been successfully demonstrated a reliable way of harvesting atmospheric water. The water vapor sorbents with high water uptake capacity and especially fast vapor sorption/desorption kinetics have become the bottleneck to a desirable clean water productivity in AWG. In this work, we developed a new nano vapor sorbent composed of a nano carbon hollow capsule with LiCl inside the void core. The sorbent can capture water vapor from ambient air as much as 100% of its own weight under RH 60% within 3 hours and quickly release the sorbed water within just half hour under 1 kW/m² sunlight irradiation. A batch-mode AWG device was able to conduct 3 sorption/desorption cycles within 10 hours during one day test in the outdoor condition and produced 1.6 kg_{water}/kg_{sorbent}. A prototype of continuous AWG device was designed, fabricated, and successfully demonstrated, hinting a possible way of large-scale deployment of AWG for practical purposes.

23 Graphical Abstract

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25 Research Highlights:

- 26 • Photothermal nano sorbents with high adsorption/desorption kinetics for atmospheric
- 27 water harvesting
- 28 • Nanosized carbon shell providing improved light-trapping and *in situ* heat generation for
- 29 uniformly and fast heating of the sorbent
- 30 • Multiple water vapor harvesting/water production cycles within one day due to the fast
- 31 kinetics
- 32 • Continuous atmospheric water generator design for potential large and automated plant-
- 33 scale deployment

34 **Keywords:** Atmospheric water harvesting, nanocapsule, vapor sorbent, photothermal material

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1. Introduction

Water scarcity is one of the greatest challenges and it is affecting two-thirds of the world's population [1-3]. Energy-intensive approaches, such as seawater desalination [4-7] and wastewater reuse [8,9], are being engaged to augment clean water production to tenuously meet the ever-growing water demand due to the fast growing population [6,8]. However, these technologies are either not affordable by impoverished communities or impractical to the communities in the landlocked regions with very limited access to water resource [10-11]. For the latter, reliance on long distance pipe transportation for fresh water becomes essential but expensive expenditure of the local economy, which is widely deemed non-sustainable [12-14]. It has been reported that more than 783 million people has no direct access to safe drinking water due to the impoverished conditions [15]. On the other hand, Earth's atmosphere always holds a substantial amount of water in the forms of vapor and droplets. The atmospheric water is estimated to be approximately 12,900 billion tons, equivalent to 6 times of water in all rivers on Earth [16]. In addition, the removal of atmospheric water is quickly compensated as an integral part of the global hydrologic cycle [17], ultimately driven by inexhaustible solar energy [17-18]. Given the fact that the seawater covers 71% of Earth's surface [16], the atmospheric water can be considered as an unconventional but easily accessible fresh water source continuously desalinated and replenished by Sun [19,20].

Several atmospheric water harvesting (AWH) technologies have been investigated during past decades, but they are met with limited success [21-24]. For example, fog harvesting requires consistently high relative humidity (RH) (i.e., typically RH 100%) [25-28]. The refrigeration-based dew water consumes electricity as high as ~1000 kWh for each cubic meter water produced in the climate conditions of RH 62%, 30 °C. When the humidity drops to 20%, the energy consumption could jump to ~5000 kWh per cubic meter water production [29-31]. Emerging nowadays is the sorption-based AWH process, which involves water vapor sorbents to harvest water vapor from ambient air and solar photothermal process to release and the condensate water is collected as fresh water product [24]. Even though the energy consumption could be high for the regeneration process of water vapor sorbent, the energy source for the regeneration of sorbent could be achieved by using low-grade energy such as solar energy or waste heat [24,31]. The advantage of the sorption-based AWG design is that the thermal sources can be used to drive the water harvesting process and thus it does not consume electricity. It works even for dry regions

with low RH, and can lead to simple, affordable, and all-in-one devices for decentralized and point-of-use (POU) year-around fresh water production, which makes it a potential solution to those who lack economical access to safe drinking water [32-36].

The thermodynamic and kinetic properties of the water sorbents are both key factors in the sorption-based AWH [37]. In 2017, Yaghi and Wang et al. successfully demonstrated the concept of use unconventional water vapor sorbent (i.e., metal-organic-framework, MOF) to extract water vapor from dry air with relative humidity as low as 20% and the water can be released by natural sunlight through photothermal process [38]. This concept was further investigated with an enlarged scale and demonstrated to be feasible in the arid climate [39,40]. In the following years, a few water sorbents with high water vapor sorption capacities and suitable absorption enthalpy have been reported [41-44]. However, the slow kinetics becomes a bottleneck: it took more than ten hours (i.e. overnight) for the sorbents to reach their water vapor saturation at ambient temperatures and several hours to release water for condensate collection under normal sunlight [41,42]. These limitations resulted the current sorbents for AWH to work only in batch mode and to complete only one sorption/desorption cycle every day. The batch mode makes it infeasible to deploy this technology to large-scale water production. Thermodynamically speaking, water vapor sorption can take place during daytime so long as there are suitable humidity and temperature. As a result, it is hypothesized that multiple or even continuous sorption-desorption cycles can be designed based on special water vapor sorbent with fast water sorption and water release kinetics. Under this premise, fresh water productivity can be enhanced with reduced weight of the sorbent.

Toward proving the hypothesis, in this work, we designed and fabricated a nano-sized photothermal water vapor sorbent with significantly enhanced vapor sorption and release kinetics. Hollow nanocapsule of ~300 nm in diameter was produced, inside which hygroscopic salt LiCl was encapsulated. In the design, LiCl acts as the active vapor sorption agent and carbon capsule serves as a container of LiCl and at the same time as the photothermal component. When packed, the space within the nano sorbent stack among the spherical nano sorbents (i.e., interparticle space) acts as the highway for water vapor transport. The advantages of the nano-design are: (1) high specific surface area for water vapor to access; (2) better light-trapping and *in situ* heat generation to minimize heat loss during heat transfer and to uniformly and fast heat up the sorbent from all directions; and (3) confinement of salt and thus sorbed water inside a solid container to avoid

interparticle water vapor channel collapse. In our design, the diffusion length of water vapor inside the capsule is less than 150 nm, which is 4-5 order of magnitude shorter than that in liquid sorbents or hydrogel-based solid sorbents [42]. The nano sorbent can capture water vapor from surrounding ambience as much as 100% of its own weight under RH 60% within 3 hours. The sorbed water can be quickly released within half hour under 1 kW/m² sunlight irradiation.

This work assembled a batch-process based AWH device using easily-accessible materials. The AWH device was tested in the outdoor condition and successfully conducted 3 sorption-desorption cycles within 10 hours during one day. The water production yield in the field test reached as high as 1.6 kg_{water}/kg_{sorbent} per day. A prototype of continuous AWG device was further fabricated based on the nano sorbent, which produced 0.86 kg water per each kg of nano sorbents in one day. Even though its apparent water production yield is not as high as the batch-based AWH device, the continuous AWH design provides a possible solution to the large and automated plant-scale deployment. To the best of our knowledge, this work reports the first sorption-based continuous AWG device. This work sheds significant light on progression from batch-based AWH process to continuous AWH process and would spark a lot of research passions to produce effective AWG for wide and practical applications.

2. Materials and methods

2.1 Chemicals and materials.

Styrene (99%) and potassium persulfate (KPS, 99%) were purchased from Acros Organics. Oleic acid was purchased from Riedel-de Haën. Phenol (99%), lithium chloride (LiCl, 98%) and hexamethylenetetramine (99%) were purchased from Sigma-Aldrich. Deionized (DI) water (18.2 MΩ, from Milli-Q system) was used throughout the experiments.

2.2 Material characterization.

Transmission electron microscopy (TEM) investigations were carried out on an FEI Titan-ST microscope. Scanning electron microscope (SEM) images were obtained on an FEI Magellan 400 microscope. Nitrogen adsorption test was measured with a Micromeritics Tristar 3020 adsorption analyzer. The X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Kratos AXIS Supra XPS spectrometer. The UV-vis-NIR spectra were obtained on a PerkinElmer Lambda 950 spectrophotometer. Water sorption properties were investigated on a NETZSCH Jupiter

simultaneous thermal analyzer (STA)-449 measurement system coupled with a modular humidity generator (MHG, ProUmid). Temperature curves and infrared (IR) images of the samples were recorded by a FLIR A655 IR camera. Thermal conductivity was measured by a set of laser flash apparatus (LFA 447 NanoFlash®, Netzsch) system with a powdery sample holder.

2.3 Fabrication of hollow carbon sphere (HCS)-LiCl nano sorbent.

Polystyrene (PS) nanospheres were synthesized as hard templates in this work. 7 ml of styrene and 188 μ L of oleic acid were mixed and dispersed in 272 mL DI water. The mixture was stirred at 50 °C for 1 hour, followed by adding 160 mg of KPS. The solution was heated to 70 °C under magnetic stirring for 5 hours. The final product was filtrated and washed by DI water. All the steps were performed under a nitrogen atmosphere.

The hollow carbon spheres (HCS) were prepared in the following steps: 225 mg of PS spheres were dispersed in 150 mL of DI water. Then 30 mL of aqueous solution with phenol (264 μ L) and hexamethylenetetramine (0.21 g) was added. The solution was transferred into a teflon-lined autoclave, heated at 160 °C for 4 hours followed by centrifugation and washed for several times with DI water (PS@PF sphere). The washed PS@PF spheres were dried in a box-type oven at 70 °C for 12 hours. The as-obtained PS@PF spheres were transferred to a tube furnace with a nitrogen atmosphere, heated to 150 °C with a ramp of 5 °C/min and dwelled for 1 hour. The temperature was then raised to 800 °C with a ramp of 5 °C/min and kept at this temperature for 2 hours, followed by cooling down to room temperature naturally [45].

The HCS-LiCl nano sorbents were obtained by immersing HCS in the saturated LiCl ethanol solution followed by vacuuming for 2 minutes. Then the HCS-LiCl was collected by vacuum assisted filtration and then dried in a box-type oven for 2 hours with a temperature of 75 °C. The infiltration process was repeated for 2 times. The weight content of carbon in the HCS-LiCl nano sorbent was estimated by the CHNS-O element analyzer (FLASH 2000, Thermo Scientific) and Energy-dispersive X-ray spectroscopy (EDS). Then the LiCl weight content was calculated by the deduction of carbon weight from the total. The volume content of LiCl in the vacancy of the HCS-LiCl was estimated based on the electron microscopic characterization (details can be found in supporting information).

2.4 Water sorption/desorption experiments.

The water vapor sorption/desorption performance of HCS-LiCl was tested by a simultaneous thermal analyzer (STA)-modular humidity generator (MHG) system under static humidity mode. The STA furnace was first heated up from 25 °C to 80 °C to dehydrate the nano sorbent and then cooled down to 25 °C for the water vapor sorption test. The sorption test was carried on for 13 hours, and then the furnace of STA was programmed to heat up to 80 °C to investigate the desorption property of the nano sorbent. Both the cooling and heating ramp was 5 °C/min. Four different humidity conditions (i.e., RH 15, 35, 60 and 80%) were investigated by purging the MHG generated wet nitrogen flow with specified RH into the STA furnace. The temperature of the nitrogen flow was maintained at 25 °C throughout the test. Water vapor absorption isotherms of HCS-LiCl were characterized by a dynamic adsorption analyzer (DVS analyzer, IGA-sorp-CT, Hiden Isochema) at 25 °C and 35 °C. Prior to the analysis, the sample was in situ pre-dried at 80 °C for 3 hours. The stability of the HCS-LiCl was investigated by a STA-MHG system for 10 dynamic absorption-desorption cycles. Each cycle consisted of a water vapor sorption section (10 h, RH 80%, 25 °C) and a water release section (1.5 h, RH 10%, 80 °C). A pre-heat cycle was applied to the sample prior the cycling test to ensure the dry state of the sample. The humidity was maintained by a MHG-generated nitrogen flow, with a constant temperature of 25 °C and an alternated RH between 10% and 80% based on the sorption/desorption sections of the experiments. The water vapor sorption behavior of HCS-LiCl nano sorbent and pure LiCl salt was also investigated in the outdoor condition. 5 g of HCS-LiCl and 5 g of LiCl salt were placed in the plastic petri dish (diameter 10 cm), and the weight change of both samples was recorded by an electric balance. The ambient condition was monitored and recorded by a LogTag humidity & temperature recorder. The outdoor test was conducted on KAUST campus, Thuwal, KSA, from 19:00-23:00 local time (GMT+3), and the sampling time was set to be 5 min.

The photothermal assisted water release property of HCS-LiCl was investigated under simulated sunlight (Oriel solar simulator, 94023A). The HCS-LiCl nanospheres were placed on a fibrous silica substrate and exposed to 60% RH atmosphere for 2 hours at room temperature (22 °C) prior test. IR camera and electronic balance were employed to record the temperature and weight change of the nano sorbent. The test was carried out under 5 different light strength (i.e., 0.7, 0.8, 0.9, 1.0, and 1.1 kW/m²).

2.5 Batch-mode AWH device fabrication and the outdoor performance measurement.

To investigate the water production performance of HCS-LiCl nano sorbent in field condition, a batch-process based, all-in-one device was fabricated. A metallic cookie box (dimension $20 \times 20 \times 5 \text{ cm}^3$) was used as the container and 12.6 g of pre-dried HCS-LiCl nano sorbent was placed inside a glass dish with diameter of 14 cm. The box was put outdoor overnight uncovered (21:00 on March 20 to 8:10 on March 21, 2019 KSA time). The device was covered with a kitchen plastic wrap next morning (8:20 am on March 21, 2019) and put on the rooftop of a town house inside KAUST campus (Thuwal, KSA). After 80 minutes sunlight irradiation, the condensed water inside metal box/on the surface of plastic wrap was collected. The box was then moved under a shaded area to prevent direct sunlight exposure to sorb water vapor from air for the next 2 hours (9:45-11:45am). The second water release and collection was conducted between 11:50-13:10. The third water vapor sorption-desorption/collection was conducted from 13:20 to 15:20. Due to sunlight strength attenuation, the device was aligned to facing the sunlight in the third cycle with extended irradiation time (15:30 to 17:30). The solar power meter was placed perpendicular to the rooftop where the experiment was conducted. The relative humidity meter recorded the value on the beginning time of two individually water vapor sorption process.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES, Agilent 5110) equipped with a charge-coupled device (CCD detector) and a charge injection device (CID detector) was used to investigate the concentration of lithium and iron in the water sample produced from the outdoor experiment. Total organic compound (TOC) analyzer (TOC-L, Shimadzu) was employed to test the TOC concentration in the same water sample.

2.6 Continuous atmospheric water generator (AWG).

A continuous atmospheric water generator (AWG) was designed and fabricated based on the HCS-LiCl nano sorbent, which included three major parts: a central rotational cylinder, a copper condenser with transparent cap, and a frame with stepper motor. HCS-LiCl nano sorbent was loaded onto the fibrous silica filter paper and mounted and wrapped around the rotational cylinder with a mass loading of 0.03 g/cm^2 (2.93 g in total). The stepper motor was set to drive the cylinder with a varied rotation rate (i.e., 0.5, 0.75, 1.5 and 4 revolution per hour, rph). The whole device was placed under simulated sunlight with a light strength of 1.0 kW/m^2 .

3. Results and discussions

In this work, we present a novel kinetic-enhanced nano-scaled water vapor sorbent for continuous AWG application. The nano sorbent is composed of a highly hygroscopic salt (i.e., LiCl) core and a porous photothermal shell (hollow carbon sphere). The hygroscopic salt is capable of sorbing a large quantity of water from the surrounding air even when the humidity is low (i.e. RH 15-35%). The hollow carbon sphere, on the one hand, holds and isolates the hygroscopic salt as a small and individual sorption unit, while generates inter-particle space for water vapor transport. On the other hand, the HCS absorbs sunlight at its surface, and in-situ heats up the saturated nano sorbent through the photothermal process. All these allow for drastic water vapor sorption/desorption kinetic enhancement, leading to it superior water harvesting and production performance.

3.1 Synthesis of HOC-LiCl nano sorbent.

Fig. 1. Schematic of HCS-LiCl nano sorbent fabrication process. Step 1: Coating of PF layer on the surface of PS hard template. Step 2: Pyrolysis of PS@PF to obtain HCS. Step 3: LiCl infiltration. Step 4: Embedment of nano sorbent to the fibrous silica substrate.

The HCS-LiCl nano sorbent was synthesized through a hard-template method by using polystyrene (PS) spheres as the core templates [45]. The PS spheres were prepared by the popular emulsion polymerization method, whose surfaces were uniformly coated with a layer of phenolic-formaldehyde (PF) via hydrothermal method (**Fig. 1**, step 1). The as-obtained PS@PF spheres were transferred to a tube furnace for high-temperature pyrolysis during which the PF layer was converted into carbon while the PS core was decomposed, leading to formation of hollow carbon spheres (**Fig. 1**, step 2). Due to the hydrophobic property of HCS after high-temperature pyrolysis, LiCl ethanol solution was used to embed LiCl salt into the as-obtained HCS under vacuum (**Fig. 1**, step 3, and **Fig. S1**). In this work, fibrous silica filter was used as the substrate to hold the HCS-LiCl nano sorbent (step 4 of **Fig. 1**, and **Fig. S2**).

237 TEM observation reveals that the average diameter of PS is ~240 nm (**Fig. 2a**). After coated with
 238 PF layer, the diameter of nanosphere increased to ~300 nm, indicating the thickness of the PF resin
 239 layer was ~30 nm (**Fig. 2b**). After pyrolysis treatment, the size of HCS was similar to that of
 240 PS@PF nanospheres (**Fig. 2c**). After LiCl was loaded, the dimension of HCS-LiCl remained almost
 241 unchanged comparing with HCS (**Fig. 2d**). **Fig. 2e** and **f** show the selective area electron diffraction
 242 (SAED) patterns of HCS and HCS-LiCl. For HCS, only dispersing diffraction rings were obtained,
 243 indicating the amorphous carbon shell. When the HCS was loaded with LiCl, an extra set of
 244 diffraction pattern indexed to (200), (111) plane of LiCl was observed [46]. The high-resolution
 245 TEM (HRTEM) image of the shell showed a typical amorphous carbon structure, consistent with
 246 the SAED result. As can be seen in **Fig. 2g**, the HCS wall shows a rough and porous surface. **Fig.**
 247 **2h** and **i** are the SEM images of HCS and HCS-LiCl, further confirming the size of nanospheres
 248 before/after the salt loading. **Fig. 2j-l** are the SEM-EDS mapping of HCS-LiCl. Since lithium
 249 element is invisible in EDS, only carbon and chloride were analyzed and mapped. The distribution
 250 of chloride perfectly matched the carbon element mapping, indicating a successful loading of LiCl.

Fig. 2. (a)-(d) TEM images of (a) PS, (b) PS@PF, (c) HCS, and (d) HCS-LiCl, respectively. SAED patterns of (e) HCS and (f) HCS-LiCl. (g) The HRTEM image of HCS. SEM images of (h) HCS and (i) HCS-LiCl. (j)-(l) SEM-EDS mapping of HCS-LiCl.

Light absorbance of HCS loaded fibrous silica filter was tested with an UV-vis-NIR spectrophotometer with silica filter as background (**Fig. 3a**). As can be seen, HCS showed an outstanding light absorbance throughout the whole spectrum ($>92\%$). The relative light absorption rate for the materials to sunlight was calculated to be 94.47% and the spectrum has been displayed in **Fig. S3**. The wetting behavior of HCS was tested indirectly through LiCl solution contact angle and chemical composition investigation. The LiCl solution contact angle of the HCS loaded fibrous silica filter was 137.5° (**Fig. S4**), indicating that the HCS was highly hydrophobic. The wetting behavior of LiCl water solution also explained the reason why a less polar solvent, ethanol, was used during LiCl infiltration process. **Fig. 3b** shows the X-ray photoelectron spectroscopy (XPS) survey spectrum of HCS, indicating 94.9% of the elements in HCS was carbon. The high-resolution spectrum of C 1s is shown in **Fig. 3c**. Five components were fitted with the C 1s spectrum, located at 284.4, 285.1, 286.4, and 288.9 eV, corresponding to the C=C (sp^2 hybridized carbon), C-C (sp^3 hybrid carbon), C-O-C, and C=O groups [47]. The atomic ratio of C/O in the HCS sample is 21.1, indicates the lack of polar groups in the material, thus lead to a hydrophobic property of HCS. The hydrophobic property towards LiCl solution of HCS is a critical factor to ensure the hygroscopic salt core can be tightly preserved inside the HCS shell even when it is turned into liquid by deliquescence. This otherwise salt leakage outside of HCS will lead to very undesirable loss of the salt and clogging of water vapor channels. The nitrogen adsorption measurement showed microporosity of HCS with a surface area of $620\text{ m}^2/\text{g}$ (**Fig. 3d**, **Fig. S5**). These results prove that HCS has an outstanding light absorption property, is hydrophobic in wettability, and has highly porous wall, all of which are desired for effective and fast water vapor sorption/desorption. Besides, the heat conductivity of the HCS stack was measured to be $\sim 0.316\text{ W}/(\text{m }^\circ\text{C})$, which could be attributed by the contact thermal resistance between the adjacent particles. Given the measured thermal conductivity, the further improvement in thermal conduction of the system can be made by using substrates with superior heat conductivity (i.e. stainless steel woven, carbon block, etc.), reducing the thickness of sorbent layer, among others.

Fig. 3. (a) UV-vis-NIR spectra of HCS loaded on the fibrous silica filter. (b) XPS survey spectrum of HCS. (c) XPS spectra of C 1s. (d) Pore size distribution of HCS. Inset is the distribution pattern in the range of 0-30 nm.

3.2 Water sorption/desorption assessment.

Theoretically, desorption of saturated sorbent is an active process where the sorbents are heated up by the external heat source. In contrast, sorption of water vapor onto the sorbent is a passive process where the diffusion kinetics of water vapor plays an important role in the overall sorption rate. In practical application, it may take only a few hours for the water sorbent to release water but a significantly longer time to recover back to its saturation state.

The water sorption behaviors of the HCS-LiCl nano sorbent were first investigated under static humidity condition. A simultaneous thermal analyzer (STA) coupled with a modular humidity generator (MHG) was employed for the water sorption/desorption assessment. At the first stage, the STA furnace was programmed to heat up to 80 °C for dehydration purpose. After the dehydration process, the furnace was cooled down to 25 °C and maintained throughout the sorption test (i.e., 13 hours). After the sorption test was completed, the furnace was heated back to 80 °C to

investigate the desorption property of the nano sorbent. Humidity generator was programmed to purge carrier nitrogen gas with pre-defined relative humidity (i.e., RH 15, 35, 60, and 80%) into the STA furnace throughout the test.

Fig. 4. (a)-(c) Static RH tests of LiCl, HCS, and HCS-LiCl under different RH conditions. The blue dash line indicates the start point of water vapor sorption process while the red dash line indicates the end of the absorption section and the beginning of the desorption section. (d)-(f) Derivative weight changes of LiCl, HCS, and HCS-LiCl under different static RH conditions.

Fig. 4a shows the static humidity test result of pure LiCl. The water uptake (i.e., weight change in Y-axis) of LiCl showed a drastic increase at RH 35, 60, and 80%. By the end of the test, the water uptake were 20.35, 106.43, 173.89, and 351.8% of the LiCl salt's own weight for 15, 35, 60, and 80% RH, respectively. LiCl salt was liquefied and its water vapor sorption equilibrium was not achieved even after 13 hours of the test. For the desorption process under 80 °C, the LiCl failed to release all of its absorbed water within the test time (i.e. 90 min). For HCS without LiCl, the weight changes due to water sorption were 1.72, 3.18, 15.76, and 17.83% of its own weight at 15, 35, 60, and 80% RH, respectively (**Fig. 4b**), which is negligible comparing with the weight change of LiCl (**Fig. 4a**). **Fig. 4c** shows the sorption behavior of HCS-LiCl. As can be seen, the sorption saturation

was achieved within 4 hours, and the final sorbed water were 22, 70, 112, and 220% at 15, 35, 60, and 80% RH, respectively. Furthermore, more than 90% of the water uptake was achieved within the first 3 hours. During vapor sorption, LiCl turns into liquid droplets and the small droplets coalesce and form bigger ones, leading to reduced contact surface area with air. Concentration-gradient drives water molecules to diffuse from the surface towards the droplet core, with Li^+/Cl^- ions diffusing in an opposite direction. As the droplets further grow in size, the diffusion length will be increased, further limiting the sorption kinetics. For the LiCl-HCS nano sorbent, the HCS limits the size of the LiCl droplet to several hundred nanometers and thus promotes the overall sorption/desorption kinetics. Unlike LiCl, a plateau was observed for HCS-LiCl under RH 35, 60, and 80%, which may attributed to the spatial limitation by HCS capsule structure and limited amount of LiCl loaded into the HCS. The sorbed water in HCS-LiCl could be very quickly released within half hour, indicating much enhanced kinetics comparing with LiCl. The weight content of carbon in the HCS-LiCl nano sorbent was estimated to be 64% (CHNS-O element analyzer) and 69.75 % (EDS) thereby the weight content of LiCl was calculated to be 30.25% and 36%. Since EDS is more accurate in measuring heavy elements, the observed weight content from EDS can be used as a comparison and show the accuracy of element analyzer (Fig. S5). The volume percentage of LiCl within the vacancy of HCS was calculated to be 17.4%, indicating more than 80% of the vacancy available for water storage (Supplementary note 1, **Fig. S6**).

The derivative weight change of all three samples were plotted and compared (**Fig. 4d-f**, **Fig. S7** and **Fig. S8**). As seen, during the sorption process, the LiCl had an almost constant sorption rate in the first 6 hours, which then slowly dropped to almost zero by the end of the test. When LiCl solution absorbs water, the concentration of LiCl decreases and its vapor pressure increases. Thus, it is noteworthy that, while the partial pressure of water vapor inside STA furnace is not changed (i.e. constant temperature and RH), the vapor sorption by the sorbent will be reduced as the sorption goes on. For HCS, a small peak in derivative weight change was observed at the beginning of the test, followed by a quick drop to zero. The derivative weight change of HCS-LiCl firstly had a rapid increase within the first 25 minutes, and then slowly dropped back to zero at ~200 min. Most importantly, the peak sorption rate of HCS-LiCl almost tripled the sorption rate of LiCl. For the desorption process, the derivative weight change of all three samples was proportional to their respective water uptake. For HCS-LiCl, the peak value of derivative weight change was double of the value of LiCl, even it had a smaller water uptake than that of LiCl, which demonstrates the

successful improvement of kinetic property. Comparing with the bulk/liquid-phased water vapor sorbent such as hydrogel or liquid desiccant, the occupation rate of the spherical nano sorbent, even densely packed as the hexagonal close packing form, is only 74%. Thus, the rest of 26% empty space (i.e., interparticle space, see Supplementary note 2 and **Fig. S9** for more details) can be used as the channels for water vapor transportation. The diffusion length can be significantly decreased to the radius of the individual sphere, which is in hundreds of nanometer. The superior performance of HCS-LiCl in both sorption and desorption can be attributed to its enlarged specific area and unblocked water vapor channel (**Fig. S10**). These properties make it a good candidate as the water vapor sorbent for AWG devices with fast water sorption/desorption property.

The water vapor sorption behavior of HCS-LiCl and pure LiCl salt was subsequently compared in the outdoor condition with an enlarged sorbent mass scale. As can be seen from **Fig. S11a**, the ambient temperature and the relative humidity during the outdoor test was $\sim 32^\circ\text{C}$ and RH 50-60%, respectively. **Fig. S11b** displays the time-dependent weight change profiles of LiCl and HCS-LiCl during the outdoor water vapor sorption test. At the initial stage (i.e. ~ 0 -25 min), the water vapor sorption rate of LiCl was slightly higher than that of HCS-LiCl. After that, HCS-LiCl nano sorbent showed a faster sorption rate. In HCS-LiCl, LiCl salt was incorporated inside the carbon capsule, while for pure LiCl sample, it started as solid phase. Thereby, at the beginning of the test before the deliquescence of LiCl solid, the pure LiCl sample showed a slightly faster kinetics than HCS-LiCl. After a short period of time, HCS-LiCl showed a better sorption kinetics, which presumably is attributed to the formation of the liquid-phased LiCl solution and consequently slow diffusion of vapor in the bulk water phase. When the test was close to the end, the slope of HCS-LiCl water uptake curve comes down, which may be due to its near saturation point. When comparing the water vapor sorption behavior from this outdoor test with the one observed from STA-MHG, the sorption rate is decreased, which may be primarily resulted from the heat/mass transfer issue in the enlarged scale [48]. However, the HCS-LiCl still shows a higher water vapor sorption behavior in the actual outdoor condition.

Water vapor sorption isotherms of HCS-LiCl were tested on a DVS analyzer to further investigate its water vapor sorption performance under varied conditions (**Fig. S12a**). Two representative temperatures in our test location, 25°C for nighttime and 35°C for daytime in a shadowed area, were investigated. As can be seen, the equilibrium water uptake from the two temperature

conditions was quite similar. The equilibrium water uptake at RH 20% is ~0.4 g/g, indicating a reasonable water sorption performance at low humidity condition. The equilibrium water uptake at the highest RH condition in this test (i.e., RH 80%) was >2.0 g/g. The results of the isotherm measurement agree well with the STA results.

The stability of HCS-LiCl was tested by a STA-MHG system for 10 sorption/desorption cycles. The sorption/desorption behavior of the HCS-LiCl is shown in **Fig. S12b**. A plateau can be observed at the end of each cycle. The unchanged water vapor sorption kinetic and water uptake capacity in each individual cycle indicates the stability of HCS-LiCl even when the humidity as high as 80% at 25 °C for 10 hours. And the structures of the spherical HCS-LiCl particles show no obvious change after the test and there is no sign of LiCl leakage (**Fig. S13**, Supplementary note 3). The results indicate that the HCS-LiCl is stable towards the water sorption/desorption cycles even when the relative humidity is as high as 80% at 25 °C.

3.3 Photothermal assisted water release.

In practical applications, it might be necessary for powder formed water vapor sorbent to be fixated onto a substrate material and assembled into an AWG device. With the device, water is released out of the sorbent at a high temperature caused by photothermal heating when it is exposed to sunlight. [49, 50] In this work, we used a fibrous silica filter as the matrix to hold the nano sorbent (HCS-LiCl@SiO₂). The dimension of sorbent loaded filter was 8 × 8 cm², composed of 0.56 g fibrous silica filter and 0.64 g of dried HCS-LiCl nano sorbent. The weight change of the HCS-LiCl@SiO₂ was real-time monitored and recorded by an electrical balance connected with a computer. The HCS-LiCl@SiO₂ was exposed to the ambient (i.e. 22 °C, RH 60%) for 3 hours, at the end of which 0.67 g water was sorbed, equivalent to 36% of its own weight at saturated state. The saturated HCS-LiCl@SiO₂ (1.87g) was exposed under simulated sunlight with a strength of 1 kW/m², under which the temperature of HCS-LiCl@SiO₂ quickly raised up to 50 °C within 2 minutes and stabilized at ~72 °C after 25 minutes. Most of the sorbed water (i.e. >90%) was released within 25 minutes, indicating a fast water release property (the “dry state” of the sample is defined by the minimum weight of the sample dried under 80 °C).

As the water evaporates, the LiCl concentration in HCS increases, resulting in a suppressed water evaporation rate, gradually reduced evaporation heat loss and increased sorbent temperature. It has to be emphasized that in this work the heat was generated by the carbon shell of HCS-LiCl nano

sorbent. In the conventional batch-processed AWH process, photothermal materials are separated with the sorbents. Heat is generated on the photothermal layer and subsequently transferred to the sorbents. Considering the existence of large heat resistance in the photothermal material-water vapor sorbent interface, heat loss during heating up the heat transfer media, and poor heat conductivity within the inner structure of AWH system, the overall utilization efficiency of solar energy is not high [32,38-42].

Fig. 5. (a) Weight change vs. temperature profile of HCS-LiCl loaded on the fibrous silica filter. (b) Stability test of the nano sorbent. The red dash line indicates 1 sorption/desorption cycle. The Y-axis indicates the water sorbed by the nano sorbent. The sunlight strength was 1 kW/m². (c) Temperature and (d) weight change profiles of saturated HCS-LiCl@SiO₂ under varied light strength.

In this work, heat is generated at the sidewall of carbon capsule and carbon is a good heat conductor. Thus the heat is locally generated and distributed homogeneously on the carbon shell with minimized heat loss, leading to fast heating of inside LiCl salt from all directions. **Fig. S14a-d** present the IR images of HCS-LiCl nano sorbents after exposure to the simulated sunlight for 0, 10, 30, and 60 minutes, respectively. A high temperature (i.e. 70 °C) can be easily achieved,

indicates the great photothermal performance of HCS-LiCl nano sorbent. The stability of HCS-LiCl@SiO₂ test was carried out by repeating the sorption/desorption process for 10 times under 1 kW/m² simulated light strength. After 10 sorption-desorption cycles test, the performance of HCS-LiCl showed almost no degradation, demonstrating its outstanding operational stability (**Fig. 5b**).

The temperature profile and water release property of HCS-LiCl were further investigated under simulated sunlight with varied light strength. A fast temperature increase can be observed under all test conditions in the first several minutes. For the light strength of 0.7, 0.8, 0.9, 1.0, and 1.1 kW/m², the temperature of the tested sample reached 39, 42, 46, 50, and 51 °C within the first 2 minutes, with their respective equilibrium temperatures at 58, 60, 65, 70, and 75 °C, respectively (**Fig. 5c**). The weight change profile is shown in **Fig. 5d**, where the Y-axis of the graph indicates the weight loss due to water evaporation relative to the saturated weight of HCS-LiCl@SiO₂. As can be seen, the weight change value at the equilibrium state for 1.1, 1.0, and 0.9 kW/m² test were quite close (i.e. ~33-36% of its own weight, 92%-100% of total absorbed water weight), indicating that the HCS-LiCl@SiO₂ can quickly release all its absorbed water as long as the sunlight strength was higher than 0.9 kW/m². For the test under 0.8 and 0.7 kW/m², by the end of the test, the weight change of HCS-LiCl@SiO₂ was ~27% (75% of total absorbed water weight), which is only slightly lower than that of the test conducted under regular solar irradiation.

The results obtained from photothermal assisted water release experiment further confirm that the HCS-LiCl is a highly efficient water vapor sorbent with fast water capture/release property and high stability. Furthermore, the ability to release water under weakened sunlight makes the HCS-LiCl nano sorbent has broad application prospects.

3.4 Batch-process based AWH device and its outdoor performance.

An all-in-one device was further assembled by using easily available commercial materials for outdoor test. The AWH device included a metallic cookie box (20 × 20 × 5 cm³) as primary container, a glass dish (diameter 14 cm) to separate the nano sorbents and collected water, and a kitchen plastic wrap as transparent window and condensation surface. During water vapor sorption process, the device was placed under a shade exposed to the ambient air. Due to the absence of the sunlight, the nano sorbent was cooled down to the ambient temperature and thus could sorb water vapor from the surrounding air (**Fig. 6a**, left). During desorption, the box was tightly sealed with the wrap and put out under direct solar irradiation. A temperature gradient was built up between

the metal box wall, air-cooled plastic wrap surface and the photothermal-heated water vapor sorbent, which provided the driving force of condensation process (**Fig. 6a**, right). **Fig. 6b-1** and **b-2** present the digital photos of the device in water vapor sorption mode and water production mode, respectively. The transmittance and reflectance UV-vis-NIR (250-2500 nm) spectra of the plastic film were tested to estimate the percentage of solar energy absorbed by the plastic film (**Fig. S15**). As can be seen, the transmittance of the plastic film maintained at ~90% in the whole range while its reflectance was around 10%. The thin film only showed a light absorbance of around 7% within the wavelength of 2250-2500 nm, meaning this film is almost transparent to the full spectrum of the sunlight.

Fig. 6. (a) Schematic of batch-processed AWH device. Left: Water vapor sorption mode, plastic wrap was removed and the sorbent was sheltered from sunlight irradiation. Right: Desorption and water-production mode, plastic wrap covered the container. (b) Digital photos of batch-process based AWH device in water-production mode (b-1), water vapor sorption mode (b-2), water collected in batch 1-3 (b-3) (red dash line indicates water level), and accumulated water collected for all three batches (b-4). (c) Weather data of March 21, 2019.

In the outdoor test, the device with 12.6 g of pre-dried HCS-LiCl nano sorbent was first kept outdoor overnight inside KAUST campus at Thuwal, KSA (21:00 March 20, 2019 to 8:10, March 21, 2019, with an average temperature of 25 °C and an average relative humidity was 60-70%, mixing ratio 12.11-13.76 g/kg_{air}) (**Fig. 6c**). The first sunlight-induced water production process was started on March 21, 2019 at 8:20 am local time (GMT+3), and around 7.7 g of water was collected within 80 minutes (8:20-9:40 am). The device was then subject to two more sorption-desorption cycle (details can be found in Method and Supplementary note 4). The 2nd and 3rd cycles produced 6.5 and 5.4 g of fresh water (**Fig. 6b-3**). In the end, the device produced an accumulative amount of ~19.6 g fresh water (**Fig. 6b-4**), which is 1.6 times the weight of the dry sorbent.

The selection of the time scale in each cycle was determined by the time efficiency and sunlight strength. Since the device relies upon solar energy as the heat source, desorption and water production mode is not operational during the night, thus the device was placed outdoor overnight to saturate its capacity. Based on the STA-MHG water vapor sorption test (**Fig. 4**), the optimized sorption rate and ~70-80% of the maximum capacity can be achieved within this time scale of <120 min. Considering the time efficiency, a duration of 2 hours was used as the water vapor sorption time for the second and third water harvesting cycle.

For the water vapor desorption process, the time scale is mainly determined by the sunlight strength during the day. The sunlight strength was sufficient to support the water release process of the sorbent during the morning and noon. However, after 15:30, the light strength quickly attenuated to an insufficient level and the photothermal-induced sorbent temperature may not enough to quickly release the absorbed water. Thus, for the first and second water harvesting process, a duration of 80 min was used for the desorption process and for the third water production cycle we chose to extend the desorption time to 120 min and align the device facing to the sunlight.

By comparison, the water production rate of HCS-LiCl in outdoor condition was only half of what predicted by the indoor STA test (~38 g, similar climate condition, 12.6 g of dried HCS-LiCl) (See Supplementary note 5 for details), indicating a significant potential for further improvement. The outdoor field experiment of HCS-LiCl demonstrates that the sorbent is capable of providing multiple water vapor sorption/water production cycles within one day. Even though the AWH device needs further improvement, the device in the field experiment still shows an excellent water production yield (i.e. 1.6 g_{water}/g_{sorbent} within one day).

The quality of water from the outdoor experiment was inspected by the ICP-OES and TOC analyzer. The concentration of lithium (from the LiCl salt in the HCS-LiCl sorbent) and iron (from the condensation chamber, i.e., cookie box) are checked. A deionized water sample generated from a Milli-Q system, a standard sample contains 5 ppm of lithium and 5 ppm of iron were used as the quality control (QC). For TOC analysis, the TOC analyzer was pre-calibrated by the TOC standard sample with a concentration of 0.10, 0.25, 0.50, 1.0, 5.0, 10 and 20 ppm, respectively. Deionized water and 10 ppm TOC standard sample were used as quality control. The quality inspection results of the water sample from the outdoor experiment are listed in **Table 1**. As can be seen, the water quality fulfills the WHO requirement. The TOC concentration is 1.96 ppm, which may resulted by the absorption of airborne organic compounds during water vapor sorption process.

Table 1. Water quality analysis of water production from the outdoor experiment

Ion concentration test		
	Iron (Fe)	Lithium (Li)
DI water	Below 0.01 ppm	Below 0.01 ppm
Water from AWG	0.02 ppm	0.01 ppm
5 ppm QC	5.01 ppm	4.98 ppm
WHO guideline	0.30 ppm	N/A
TOC test		
	TOC concentration	
DI water	0.12 ppm	
Water from AWG	1.96 ppm	
10 ppm QC	10.09 ppm	

3.5 HCS-LiCl based continuous AWG device.

The conceptual design of the continuous AWG device is shown in **Fig. 7a** and **Fig. S16**. **Fig. 7b** presents a digital photo of the real device. The dimension of the device is $11.15 \times 10.75 \times 10.00$ cm³, with a rotational cylinder encapsulated ($\Phi=42$ mm, $L=74$ mm). 2.93 g of sorbent was homogeneously loaded on the rotational cylinder with loading density of 0.03 g/cm² (Details can be found in Supplementary note 6). In this continuous device, the rotational cylinder loaded with water vapor sorbent is placed between two grooved frames. The top sector of the rotational cylinder is exposed to the sunlight and condensation chamber to release water, while the bottom sector is exposed to the ambient to harvest water vapor (**Fig. 7b**). The incident sunlight penetrates the transparent cap and irradiates on the top sector of the rotational cylinder (**Fig. 7c**). The water-saturated water vapor sorbent is quickly heated up and releases water in vapor phase. The released

water vapor is condensed on the top plastic cover and on the sidewall of copper condensation chamber (**Fig. 7d**), the condensed water droplets on the sidewalls slide down to the PTFE collector and direct to the water outlet. The dehydrated water vapor sorbent is rotated to the bottom side along with the rotation of the center cylinder, and starts the next water vapor sorption and photothermal-assisted water release cycle. The water content and temperature profile of water vapor sorbent are colored by two concentric rings.

Fig. 7. (a) Schematic of cross sectional view of the sorption-based continuous AWG prototype. (b)-(d) Digital photo of final assembled AWG device, AWG device in operation, and water condensed on the side wall of the condensation chamber, respectively. (e) Cumulative water production yield of AWG device under varied cylinder rotation rate. (f) IR image of water vapor sorbent exposed to the sunlight under varied cylinder rotation rate. (g) Temperature profile of water vapor sorbent exposed to the sunlight under varied cylinder rotation rate. The simulated sunlight strength in this test was 1 kW/m².

The prototype was tested in the lab condition where environmental conditions are controlled by the centralized heating, ventilation, and air conditioning (HVAC) system. The temperature and the relative humidity is maintained at 22 °C, 60%, respectively. Given the small size of the device and

the outstanding heat conductivity of metal condensation chamber, the condenser temperature was similar to the environmental temperature (i.e., 22 °C). For each rotation rate condition, 3 batches of the experiment were conducted under a specific collection duration (i.e., 1, 2, and 4 hours). A pre-weighted filter paper was used to collect the condensed water by the end of each test. The water production yield of each individual test can be calculated from the weight difference of the filter paper. The water production performance of the continuous AWG prototype is compared in **Fig. 7e**. A quantity of 0.24, 0.30, 0.09, and 0.02 g water was produced during first hour with the cylinder rotation rate of 0.50, 0.75, 1.25, and 4 revolution per hour (rph), respectively. These trends can be observed even when the collection duration time was extended to 2 and 4 hours. By the end of the 4-hour test, 0.69, 1.25, 0.3, and 0.035 g of water was collected under rotation rate of 0.5, 0.75, 1.5, and 4 rph, respectively. A detailed list of water harvesting rate in the varied conditions has been displayed in **Table 2**. An IR camera was used to observe the temperature of the water vapor sorbent under sunlight irradiation with varied rotation rate (**Fig. 7f**). The dash line in each of the IR images covered the “cold” region (i.e., less than 40 °C) of the water vapor sorbent, and the size of “cold” region expanded along with the increased cylinder rotation rate (Supplementary note 7). The temperature gradient across the sorbent surface (green line across the IR image) also confirmed the temperature difference under varied rotation rate (**Fig. 7g**). The desorption rate of water from the sorbent was lower due to the lowered temperature under faster rotation rate. However, if the rotation rate of the cylinder is too slow (e.g., 0.5 rph), on the one hand, the water vapor sorbent exposed to the sunlight will be exhausted due to over exposure. On the other hand, the adjacent water vapor sorbent is collaterally heated up and thus releases water before moving into the condensation chamber due to the internal heat conduction, thus leading to a decreased water production yield. The water production yield was estimated to be 0.84 g_{water}/g_{sorbent} within 8 hours. Ongoing effort is being made on improving the overall efficiency of the device.

Table 2. The detailed water harvesting rate in the varied test conditions.

	0.5 rph		0.75 rph		1.5 rph		4 rph	
Collection time (h)	Rotational cycles (r)	Harvested water (g)	Rotational cycles (r)	Harvested water (g)	Rotational cycles (r)	Harvested water (g)	Rotational cycles (r)	Harvested water (g)
1	0.5	0.24	0.75	0.3	1.5	0.09	4	0.02
2	1.0	0.45	1.5	0.61	3	0.15	8	0.031
4	2.0	0.69	3.0	1.25	6	0.3	16	0.035

In summary, the sorption-based continuous AWG device we presented in this work can harvest water from the air continuously. To the best of our knowledge, this is the first sorption-based continuous AWG device ever reported, whose performance needs further improvement.

4. Conclusion

In conclusion, a nano-scaled photothermal water vapor sorbent with a spherical photothermal shell and a hygroscopic salt core was designed and synthesized. The water vapor sorption and desorption kinetics were largely enhanced comparing with the previously reported water vapor sorbents. The sorbent is capable of absorbing water vapor from air as much as 100% of its own weight within 3 hours under RH 60%. The absorbed water can be quickly released within 30 minutes under 1 kW/m² sunlight irradiation. A batch process-based AWG demonstrated the superior water production yield as much as 1.6 kg water per kilogram sorbent per day, which was enabled by its multiple atmospheric water harvesting cycles within one day. A sorption-based conceptual prototype of continuous AWG device was assembled and investigated in the laboratory condition. The continuous production of clean water was successfully demonstrated.

Declaration of interests.

Peng Wang, Renyuan Li, and Yusuf Shi have a patent application related to the work presented in this paper.

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Appendix A. Supplementary data

Schematics of LiCl infiltration process. SEM image of HCS-LiCl@SiO₂. The relative light absorption rate for the sample to sunlight. Wetting behavior of LiCl water solution on the HCS-LiCl@SiO₂. Nitrogen sorption isotherm of HCS. Calculation of the volume percentage of LiCl in the HCS vacancy. Full-range curve of derivative weight change. Zoom-in plot of water vapor absorption section. Calculation of the dimension of interparticle space. Schematics of sorption/desorption behaviors of nano sorbent and bulk-phased sorbent. Water vapor sorption behavior of HCS-LiCl and LiCl in outdoor condition. Water vapor sorption isotherms of HCS-LiCl. STA-MHG based stability test results. SEM observation of HCS-LiCl under varied conditions. IR images. UV-vis-NIR spectrum of plastic film used in the field test. Experimental details and discussion on the batch-mode AWG. Estimation of the water production yield of HCS-LiCl nano sorbent under STA test condition. Detailed assembly of continuous AWG device. Device design of continuous AWG. Calculation of sorbent exposure time under sunlight in the continuous AWG device.

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