Atmospheric water harvesting (AWH) offers a solution for efficiently extracting water from the air. In this protocol, we detail the steps to develop a composite sorbent loaded with hygroscopic salts and lithium chloride (LiCl) and based on hydrogel, acrylamide monomer (AM), and carbon nanotubes (CNTs). We describe a streamlined experimental approach for the synthesis of the honeycomb-optimized hydrogel-based composite adsorbent (PCLG) by in situ polymerization. The produced sorbent exhibits ultra-high adsorption/desorption capacity per unit volume and low-temperature desorption.

Publisher’s note: Undertaking any experimental protocol requires adherence to local institutional guidelines for laboratory safety and ethics.
Protocol for atmospheric water harvesting using in situ polymerization honeycomb hygroscopic polymers

Chunfeng Li,1,3 Jiayun Wang,1,4,* Chaohe Deng,1 Ruzhu Wang,2 and Hua Zhang1

1Institute of Refrigeration and Cryogenics, University of Shanghai for Science and Technology, 516 Jungong Road, Shanghai 200093, China
2Institute of Refrigeration and Cryogenics, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China
3Technical contact: 212210111@usst.edu.cn
4Lead contact
*Correspondence: jywang@usst.edu.cn

SUMMARY
Atmospheric water harvesting (AWH) offers a solution for efficiently extracting water from the air. In this protocol, we detail the steps to develop a composite sorbent loaded with hygroscopic salts and lithium chloride (LiCl) and based on hydrogel, acrylamide monomer (AM), and carbon nanotubes (CNTs). We describe a streamlined experimental approach for the synthesis of the honeycomb-optimized hydrogel-based composite adsorbent (PCLG) by in situ polymerization. The produced sorbent exhibits ultra-high adsorption/desorption capacity per unit volume and low-temperature desorption. For complete details on the use and execution of this protocol, please refer to Wang et al. (2022).

BEFORE YOU BEGIN
The following protocol describes the specific steps and typical characteristics of the hydrogel-based composite sorbent PCLG, which equips with ultra-high adsorption/desorption capacity per unit volume and low-temperature desorption. The developed adsorbent PCLG achieved a high water collection capacity of 3.97 g/cm³ and 2.55 g/g at the desorption performance of 45°C and 40% relative humidity (RH).

The high adsorption capacity, high adsorption density, and cycle stability hydrogel sorbents have been considered in recent years for the use of AWH (Ejeian and Wang, 2021). The protocol develops a composite sorbent loaded with hygroscopic salts, lithium chloride (LiCl), based on hydrogel, acrylamide monomer (AM), and carbon nanotubes (CNT). The protocol provides a streamlined experimental method for designing and developing gel-based composite adsorbents, such as PAM-CaCl₂ (Li et al., 2018).

Preparation of carboxylated CNTs

© Timing: 5 h

The preparation of sorbents requires a certain amount of carboxylated CNTs, and the total amount varies according to the size and weight of the prepared sorbents. The mixed acid solution can dissolve the impurities on CNTs, purify the product, and carboxylate the carbon nanotubes. The carboxylated CNTs have stronger hydrophilicity and can be better dispersed in an aqueous solution. The material dosage in the following experimental steps is based on the preparation of 5 g carboxylated CNTs.
1. Transfer 10 mL nitric acid with a concentration of 70% and 30 mL sulfuric acid with a concentration of 98% with a pipette gun in a beaker to prepare the mixed acid solution (Figure 1A).

**Note:** Changing pipetting heads of different sizes helps to complete the operation quickly.

**Note:** Clean the beaker or test tube after use.

**CRITICAL:** The operation should be done in the fume hood. Wear goggles and rubber gloves when using strong acid (Figure 1B), and strictly follow the fume hood practical guidelines.

2. Weigh 5 g of CNTs using the precision balance (Figure 1C) and transfer to the acid solution.

3. Pour the mixture into the flask and condense reflux at 70°C for 4 h (Figure 1D).

**Note:** The unit’s operation of condensate reflux and removal should be carried out in the fume hood to avoid the harmful gas from the experiment being discharged into the laboratory.

**CRITICAL:** Pay attention to the smooth flow of condensate water; Avoid oil bath burns when removing the condensate reflux unit.
4. Dilute the condensate solution with deionized water, then centrifuge it three times at 12,000 rpm (15,805 \times g) (Figure 1E). The recommended time for each centrifugation is about 5 min.

**Note:** The quality of the solution placed in each tube of the centrifuge should be the same to avoid incomplete centrifugation and damage to the machine.

**Note:** If the precipitation in the centrifugal tube is not apparent, multiple centrifugations or speed fine tuning can be carried out.

△ **CRITICAL:** Drop the mixed solution into excessive water when diluting the solution. Do not drop water into the mixed solution to avoid splashing.

5. Transfer samples from the bottom of the centrifuge tube, dry them inside an oven at 120 °C (8 h) and seal them in the reagent tube (Figure 1F).

△ **CRITICAL:** Avoid excessive wind speed. The weight of carbon nanotubes is light and easy to blow away, causing quality loss.

**Note:** The production of carboxylated CNTs is about 75%.

**Pause point:** Carboxylated CNTs can be stored at ambient conditions (25 °C) once carefully sealed. The recommended maximum storage time is one week.

---

**KEY RESOURCES TABLE**

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| **Chemicals, peptides, and recombinant proteins** |
| Acrylamide          | Sigma-Aldrich | CAS: 79-06-1 Product Number for Sigma-Aldrich: A8887-100g ≥ 99% |
| Ammonium persulfate | Macklin | CAS: 7727-54-0 Product Number for Macklin: A801035-500g, ≥ 98.5% |
| N,N-Methylenebisacrylamide Bis-acrylamide | Macklin | CAS: 110-26-9 Product Number for Macklin: N917391-50g, ≥ 99% |
| N,N,N',N'-Tetramethyleneethylenediamine | Macklin | CAS: 110-18-19 Product Number for Macklin: N818999-25mL, ≥ 99% |
| Lithium chloride    | Sigma-Aldrich | CAS:7447-41-8 Product Number for Sigma-Aldrich: 310468-500g, ACS reagent, ≥ 99% |
| Carbon nanotube     | Sigma-Aldrich | CAS:308068-56-6 Product Number for Sigma-Aldrich: 900711-5g, ≥ 99% |
| Deionized water     | N/A | 18 mΩ |
| **Other**           |
| Constant temperature heating magnetic stirrer | Gongyi Yuhua Co., Ltd. | DF-101S |
| High-speed Centrifuge | Hunan Xiangyi Laboratory Instrument Co., Ltd | H2050R |
| Drying Oven         | Shanghai Zuoke Instrument Equipment Co., Ltd | DHG-9240A |
| Ultrasonic Cell Grinder | Shanghai Bilang Instrument Manufacturing Co., Ltd. | BiLON-1000Y |
| Magnetic Stirrer     | Shanghai Meiyingpu Instrument Manufacturing Co., Ltd. | 524G |
| Precision Electronic Balance | Sartorius | SQP-PRACTUM224-1CN |
MATERIALS AND EQUIPMENT

### Gel Solution

| Reagent                                           | Final concentration | Amount  |
|---------------------------------------------------|----------------------|---------|
| Carbon nanotubes (CNTs)                           | 0.15%                | 4.5 mg  |
| Lithium chloride (LiCl)                          | 50.3%                | 1.51 g  |
| Acrylamide (AM)                                  | 20%                  | 0.6 g   |
| Ammonium persulfate (APS)                        | 0.3%                 | 9 mg    |
| N,N-Methylenebisacrylamide Bis-acrylamide (MBAA) | 0.2%                 | 6 mg    |
| N,N,N,N'-Tetramethylethylenediamine (TEMED)      | 0.001%               | 30 µL   |
| dH2O                                              | N/A                  | 3 mL    |
| **Total**                                         | **N/A**              | **3 mL**|

**Note:** Prepared gel solution can be stored at 10°C for up to 48 h. The solution can also be stored at lower temperatures, as long as it does not cause the solution to freeze.

△ **CRITICAL:** Acrylamide has certain carcinogenicity; wear organic filter masks and protective gloves during operation.

STEP-BY-STEP METHOD DETAILS

#### Preparation of gel solution

© **Timing:** 0.5 h

The following steps describe the detailed preparation processes of gel solution by in-situ polymerization, as shown in Figure 2.

1. Weigh 4.5 mg of Carboxylated CNTs and disperse in 3 mL deionized water by ultrasonic cell grinder (Figure 2A).

**Note:** Parameter setting of ultrasonic disperser: start 1.5 s, stop 3 s; The diameter of the amplitude rod is 3 mm, and the power is 400 W; Ultrasound time is 120 minutes.

**Note:** Pay attention to observe whether the solution splashes during ultrasonic dispersion.

△ **CRITICAL:** The ultrasonic process promotes water evaporation, so the mass should be weighed before and after processing. Evaporated water should be replenished after ultrasonic dispersion to ensure consistent quality of reagents.

2. Weigh 1.51 g of anhydrous lithium chloride by using precision balance and transfer to the CNTs solution.

△ **CRITICAL:** The weighting and transfer process must be as quick as possible to minimize water vapor sorption by anhydrous lithium chloride.

3. After dissolving LiCl in CNTs solution completely and cooling it to room temperature, place the beaker in an ice bath (Figure 2B).
   a. Maintain ice bath temperature at 5°C.

**Note:** Reagent addition needs to be done in an ice bath until the gel solution is prepared.
4. Add 0.6 g AM to the CNT-LiCl solution in the beaker and stir slowly until completely dissolved (Figure 2C).

△ CRITICAL: Acrylamide has certain carcinogenicity, wear protective gloves and organic filter masks during operation. CNT-LiCl solution is a black liquid; carefully observe whether AM is completely dissolved.

5. Add 9 mg APS and 6 mg MBAA into the AM-CNT-LiCl solution successively and stir slowly until reagents are entirely dissolved (Figure 2C).
   a. Use high precision electronic balance to ensure accurate mass weighing.

△ CRITICAL: Ensure that all reagents are poured into the solution to avoid sticking to the beaker wall and weighing paper due to the low reagent dose.

6. Place the above gel solution directly in the reagent tube and seal (Figure 2D). Alternatively, drop 30 μL TEMED into the solution, stir well, and stand at room or low temperature to form a flake hydrogel (Figure 5A).
CRITICAL: Stir evenly after dropping TEMED to ensure the same gel formation rate and good hygroscopicity.

Note: The final hydrogel sample is black, flake, and soft in texture.

Pause point: Prepared gel solution can be stored at 10°C for up to 48 h. The recommended best usage is within 24 h.

Preparation of honeycomb hydrogel

Timing: 12 h

In this part, we describe the preparation of honeycomb hydrogel by a special mold. The mold shown here is an example. You may set your own hydrogel mold according to your study design.

7. Transfer 12 mL of the gel solution (PCL) prepared in the previous step and pour it into the 60 x 60 mm mold (Figure 3A).

Optional: Any shapes and sizes are available and can be chosen according to the requirements. Here is an example of a removable honeycomb mold (Figure 3B).

△ CRITICAL: The edge of the mold should be sealed to avoid solution leakage.

8. Drop Evenly 120 μL TEMED into the above mold and mix well using a mixing bar.
9. Carefully insert into the hole-making molds and leave overnight at ambient conditions (25°C) (Figure 3B).

Preparation of PCLG

Timing: 12 h

This step describes the approach to dissociate mold to obtain honeycomb hydrogel.

10. Remove mold (Figure 4A).
   - Carefully remove the acrylic sheet around the mold.
b. Before pulling out the mold, reduce the adhesion between the hydrogel and the hole-making mold, and then pull out the hole-making mold.

11. Hang the hydrogel in the oven with a clamp, which lasts 12 h, and set the temperature at 120°C (Figure 4B).

⚠️ CRITICAL: The oven temperature is high, and operators need to wear anti-scald gloves to avoid scalding.

Note: Honeycomb hydrogels are black blocks with neat circular array channels in the middle.

**EXPECTED OUTCOMES**

This protocol allows for the synthesis of PAM-CNT-LiCl composite hydrogel. The expected results will be consistent with our previous paper on Cell Reports Physical Science (Wang et al., 2022), and some criteria listed below.

**Expected visual outcomes**

PCLG has the advantages of strong water absorption, stable properties, and a low water desorption temperature. It can also be processed into a target geometry by changing the vessel’s shape in which the crosslinking reaction occurs. The visual appearance of PCLG is shown in Figure 5A. Once dry, it forms a rugged and durable black solid. A sample of PCLG fractured at the temperature of liquid nitrogen shows numerous surface pores, which provide fast channels for gaseous and liquid water to enter the hydrogel (Figure 5B). PCLG has many macroporous structures inside with a 28 μm average pore diameter tested by mercury intrusion. Compared with other porous sorbents, the density of PCLG is 1.56 g/cm³, which is about 2.5 times that of MOF-801 (0.617 g/cm³), and the tighter internal organization of PCLG gives it lower resistance to heat transfer and water diffusion.

**Expected vapor isothermal sorption isotherms of PCLG**

The water vapor adsorption experiment of PCLG was carried out in a constant temperature and humidity box, and an electronic balance was adopted to measure the weight of the sorption samples. The gels were tested under 5°C & 75%, 15°C & 75%, 25°C & 75%, 35°C & 75% working conditions as shown in Figure 6A. It can be seen that all adsorption curves have similar trends under different working conditions, as shown in Figure 6B.
The desorption kinetics of PCLG during desorption was tested by STA 449 Netzsch, and experimental results are shown in Figure 7. According to the experimental values, the desorption kinetic curve is fitted by the linear driving force (LDF) model, and the desorption rate coefficient of the adsorbent at 60°C is obtained.

Expected dynamic water uptake performance under various relative humidity

In the water harvesting cycle, the mass of water harvested per gram of material (g/g) is defined as the difference between the amount of water absorbed and the residual amount of water in the material after desorption. As shown in Figure 8, the optimized PCLG (1.5 mg/mL CNTs, 33% LiCl) achieved 5.76 g/cm² (3.70 g/g) water uptake under humid conditions at 35°C and 3.8 kPa for 7 h and retained 1.79 g/cm² (1.15 g/g) water in the material at 45°C 40%RH and 3.8 kPa for 5 h, meaning that water
was harvested at 3.97 g/cm³ (2.55 g/g). For semi-humid conditions, PCLG captured 2.33 g (3.63 g/cm³) of water at 30°C and 2.3 kPa and harvested 1.54 g (2.40 g/cm³) of water after the 52°C desorption phase. Under arid conditions, the hydrogel harvested water at 1.12 g/cm³ from 1.10 g/g (1.80 g/cm³) water uptake at 30°C and 1.3 kPa and left a residual water mass of 0.38 g/g (0.68 g/cm³) after the 52°C desorption phase.

Expected cyclic sorption-desorption performance
To demonstrate cycling stability of the sorbents, 10 times water sorption-desorption cycling tests of PCLG were repeated under 25°C, 2.3 kPa (75% RH) for sorption and 60°C, 2.0 kPa for desorption, with no significant sign of degradation in performance shown (Figure 9).

Figure 7. Isothermal desorption kinetics of PCLG under 60°C temperature
Reprinted from Cell Reports Physical Science, Wang et al., High yield and scalable water harvesting of honeycomb hygroscopic polymer driven by natural sunlight with permission from Elsevier.

Figure 8. Dynamic sorption performance of PCLG at different working conditions of 1.2 kPa, 2.3 kPa, and 3.8 kPa
Reprinted from Cell Reports Physical Science, Wang, et al., High yield and scalable water harvesting of honeycomb hygroscopic polymer driven by natural sunlight with permission from Elsevier.
LIMITATIONS

In comparison with MOFs, Hydrogels (PCLG) are relatively low-cost and easier to prepare, but the sorption kinetics of these materials is slower in arid climates (RH< 30%). We noticed that by molding the pores (such as the honeycomb structure), the porosity of the gel material could be increased, resulting in lower resistance to water vapor transmission. However, this void ratio requires the theoretical model (Wang et al., 2022) to calculate the best result, and the situation of this agreement may not apply to all similar gels.

TROUBLESHOOTING

Problem 1

The water uptake of the sorbent is more than 10% attenuation than that reported above (Figure 8).

Potential solution

The ideal salt content of PCLG sorbents is 50 ± 1 wt%, and the salt content affects the final sorption performance, so it is important that the process of adding salt solution is successful. (Figure 2) If not, check the following two points.

Carefully check the concentration of lithium chloride solution when preparing the salt solution. If anhydrous lithium chloride is incorrectly weighed or exposed to air for too long, the hygroscopic salt can absorb a form of water vapor and form lithium chloride hydrate. This can lead to weight deviation, resulting in lower lithium chloride content (Figure 2). Due to excessive impurities in the lithium chloride reagent selected, the lithium chloride solution is still turbid after prolonged stirring, so the reagent provider should be changed.

Problem 2

No hydrogel or uneven hydrogel was formed in the gel solution after 12 h in the mold.

Potential solution

Several steps will result in solution polymerization failure. Check the following four points.
A large amount of reaction heat will be released when AM is polymerized. If it is not cooled in time, a large number of insoluble substances will be produced, so the operation of adding reagents must be carried out in an ice bath (Figure 2B). Due to uneven stirring, the reagents were not completely dissolved or hung on the wall during transfer. Stir as much as possible to dissolve completely for each reagent configuration operation. The ambient temperature of the gel solution is too high, which should be kept at about 25°C (Figure 3). The initiator APS can promote the gel; too much will lead to local polymerization too fast and make it difficult to form a whole. Strictly adhere to the reagent ratio given in the protocols.

**Problem 3**
Carbon nanotubes don’t disperse uniformly in deionized water (Figure 2A).

**Potential solution**
The CNTs samples are small, hard black particles that can be ground in a mortar prior to sonication to make it easier to disperse CNTs uniformly in water.

**Problem 4**
The yield of carboxylated CNTs obtained by centrifugation was low (Figure 2E).

**Potential solution**
Increase the number of centrifugations or use suction filtration to collect CNTs when experimental conditions are available.

**Problem 5**
The hydrogel (PCLG) removed from the mold always crumbles (Figure 4A).

**Potential solution**
The mold edges are not sealed, resulting in loss of solution and uneven gel formation. Please add sealing measures. When the number of pore-making is large, the hydrogel and the pore-making mold adhere firmly, so the adhesion between them should be reduced as much as possible first to avoid the damage of the pore and hydrogel rupture.

**RESOURCE AVAILABILITY**

**Lead contact**
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, J.Y. Wang (jywang@usst.edu.cn).

**Materials availability**
PCLG generated in this study will be made available on request, but we may require a payment or a completed materials transfer agreement if there is potential for commercial application.

**Data and code availability**
This study did not generate or analyze datasets or code.

**ACKNOWLEDGMENTS**
The authors gratefully acknowledge the support and funding for this research, which is sponsored by the National Natural Science Foundation of China (no. 52006145), Shanghai Sailing Program (no. 20YF1431500), Shanghai Morning Light Project (no. 19CG54), and the Central Guidance on Local Science and Technology Development Fund of Shanghai City (no. YDZX2021310003002).
AUTHOR CONTRIBUTIONS
C.L., C.D., and J.W. conceived the experiments. C.L. and C.D. designed and optimized the protocols. J.W. and R.W. revised the manuscript and guided the overall project. J.W. and H.Z. funded the project. All the authors discussed and reviewed the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

REFERENCES
Ejeian, M., and Wang, R.Z. (2021). Adsorption-based atmospheric water harvesting. Joule 5, 1678–1703. https://doi.org/10.1016/j.joule.2021.04.005.

Li, R., Shi, Y., Alsaedi, M., Wu, M., Shi, L., and Wang, P. (2018). Hybrid hydrogel with high water vapor harvesting capacity for deployable solar-driven atmospheric water generator. Environ. Sci. Technol. 52, 11367–11377. https://doi.org/10.1021/acs.est.8b02852.

Wang, J., Deng, C., Zhong, G., Ying, W., Li, C., Wang, S., Liu, Y., Wang, R., and Zhang, H. (2022). High-yield and scalable water harvesting of honeycomb hygroscopic polymer driven by natural sunlight. Cell Rep. Phys. Sci. 3, 100954. https://doi.org/10.1016/j.xcrp.2022.100954.