# Supporting Information

## A Novel Dual-network Structure of Hydrogel Microspheres for Efficient Atmospheric Water Collection

## Contents

## 1.experimental section

### 1.1 Materials

All chemicals were used as obtained without modification. [2-(Methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (DMAPS, ≥97%), N,N′-Methylenebis(acrylamide) (BIS, 99%), carbon nanotube（CNT）and N,N,N′,N′-Tetramethylethylenediamine (TEMED, 96%) were obtained from Aladdin. Potassium persulfate (KPS, ≥98%) was purchased from Beijing Bailing Wei Technology Co., LTD. Lithium chloride (LiCl, 99%), sodium sulfite (SDS), calcium chloride ($CaCl_2$, 96%) and sodium alginate (SA, M/G=2:1，≥99%) were purchased from Macklin.

### 1.2 Preparation of CA/PDMAPS/CNT/Salt

First of all, sodium alginate was dissolved in deionized water at 80 ° C, and then DMAPS and BIS were added continuously, stirring continuously until completely dissolved. Then the carbon nanotubes were dispersed into the mixed solution, ultrasounded for 30 minutes, and passed into $N_2$. The prepared solution was carefully dropped into a $CaCl_2$ /KPS/SDS solution to initiate polymerization and then dropped into TEMED for gelation. The detailed composition of the reaction mixture is shown in Table S1. After a reaction at room temperature for 24h, the hydrogel microspheres were filtered and cleaned several times with deionized water to remove unreacted monomers and excess $CaCl_2$.

In order to load hygroscopic salts into the hydrogel microspheres, the cleaned microspheres were soaked in a very small amount of saturated LiCl. After 24h, the microspheres were cleaned with ethanol for several times. We selected hydrogel microspheres with a diameter of about 3mm and dried them overnight in an oven at 120 ° C. The obtained samples and microspheres are stored in sealed petri dishes for subsequent use.

### 1.3 Swelling Test

$CaCl_2$ exists in the preparation of CA/CNT and CA/PDMAPS/CNT hydrogels, and the internal $CaCl_2$ cannot be completely removed through deionized water washing, which will greatly affect swelling experiments. Therefore, we first selected undried CA/CNT, CA/PDMAPS/CNT and PDMAPS/CNT hydrogels and soaked them in deionized water for 12h. The hydrogel microspheres were then filtered and dried. The dried CA/CNT, CA/PDMAPS/CNT and PDMAPS/CNT hydrogel microspheres were divided into six groups. Finally, different concentrations of salt solutions were used for swelling experiments. The swelling ratio of microspheres can be calculated using the following formula:

$$\textit{Swelling ratio} = \frac{m_1 - m_0}{m_0}$$

Where $m_0$ and $m_1$ represent the weight of the microspheres after drying and soaking respectively. All tests were measured for least 3 times to obtain an error analysis and a reproducibility analysis.

### 1.4 Water Adsorption Experiment

The prepared CA/CNT/LiCl, PDMAPS/CNT/LiCl, CA/PDMAPS/CNT/LiCl hydrogel microspheres were dried, and then divided into three groups with five microspheres in each group, with their dry weights recorded. The parameters of the artificial climate incubator were set at 22°C with a controlled relative humidity (RH) range of 30–90%. The petri dish containing the samples was placed inside the incubator, and the sample weights were periodically measured. Each experiment was repeated for at least five times to ensure reproducibility and minimize experimental errors. Water absorption was calculated using the following equation:

$$\textit{Water uptake} = \frac{m_2 - m_1}{m_1}$$

Where $m_1$ represents the initial mass of the dried samples, and $m_2$ represents the mass of the samples after water absorption.

### 1.5 Solar-driven Desorption Experiment

First of all, 10 samples of CA/PDMAPS/CNT/LiCl hydrogel microspheres were selected and dried in an oven at 110°Cfor 4h. The dried samples were transferred to a chamber with a constant temperature of 22°C and a relative humidity of 90% for hygroscopic absorption, which stopped when its hygroscopic capacity reached 1g/g. A solar simulator (94083A) was used to simulate sunlight, and the light intensity was changed by adjusting the output power and distance (600w /$m^2$, 800w /$m^2$, 1000w /$m^2$, 1200W/$m^2$). The quality of hydrogels was monitored at intervals of 2min.

### 1.6 Cyclic Testing

For the first cycle, 10 CA/PDMAPS/CNT/LiCl hydrogel microspheres were selected and dried in an oven at 120°C for 4h. It was then placed in an artificial climate simulation chamber (22°C, RH = 60%) for adsorption until an equilibrium was reached, ensuring a complete hydration and activation of the materials. This was followed by desorption at 80°C, 0%RH. This cycle was repeated for 30 times with the adsorption and desorption times systematically optimized throughout the experiment.

### 1.7 Outdoor Measurement

We constructed a simple atmospheric water collection device using two PET hemispheres, each with a radius of 7 cm. From 8:00 PM to 7:00 AM (May 20–21, 2024), 5g of CA/PDMAPS/CNT/LiCl hydrogel microspheres were exposed to ambient air to capture atmospheric water (location: China University of Mining and Technology, Beijing, China).

The weight changes of the hydrogel microspheres were monitored using a precision electronic balance, while temperature and humidity were recorded with a DL336001 hygrograph (Deli Group Co., LTD., China) under real-world environmental conditions.

During the daytime (8:00 AM–6:00 PM), the hydrogel microspheres were transferred to the atmospheric water collection device for desorption. Sunlight intensity was measured using an SM2065-SOLAR solar power meter (Xingbao Instrument, China), and the weight of the fresh water collected was record using the precision electronic balance.

### 1.8 Characterization

Scanning electron microscopy (SEM) images were made using a FEI Nova Nano 450 instrument, which used its energy dispersion spectrometer (EDS) function, with an operating distance of 15mm and an operating voltage of 15kv. Before SEM analysis, the samples were bonded to a sample table with conductive adhesive and gold spraying was performed. An EDS test was performed under the condition with the working distance of 15mm and a working voltage of 15kv. The samples were analysed using Fourier infrared spectroscopy (FTIR) with a Nicolet 6700 infrared spectrometer. 64 scans were collected at a resolution of 4cm$^{-1}$, with a wavelength range of 4000-400cm$^{-1}$. The absorbance of the composites was quantitatively determined using UV-VIS-NIR (UV-VIS-NIR) spectroscopy through a UH-4150 UV-vis spectrophotometer. The measurement parameter ranges from 200-nm to 2500nm. The purity of the collected water was tested using an Avio 200 inductively-coupled plasma emission spectrometry instrument (ICP-OES). The thermal behaviour of the samples was analysed using a thermogravimetric analysis (TGA) at 20~800°C, 10°C/min and $N_2$. The salt content of hydrogel microspheres before and after cycling was measured using ICP-OES (inductively coupled plasma optical emission spectrometry).

## 2. Supplementary Picture

**Table 1.** Sample preparation materials list

**Figure S1.** Synthesis method and the chemical structure of CA/PDMAPS/CNT/LiCl hydrogel microspheres

**Figure S2.** Sample picture when the quality ratio of SA: DMAPS is less than 1:6

**Figure S3.** Swelling rate of different samples in a 0.1g/mL LiCl solution

**Figure S4.** Water uptake of different samples at RH= 90%

**Figure S5.** Samples S1 and S2 were loaded with LiCl drying images of the same quality

**Figure S6.** The $Ca^{2+}$ content of CA hydrogels was obtained after soaking in LiCl at different concentrations.

**Figure S7.** LiCl leakage experiment. (a) CA/PDMAPS/CNT/LiCl and CA/CNT/LiCl hydrogels were placed on copper plates and blank groups were set. (b) Copper surface after 14 days at 22°C and RH= 60%.

**Table 1.** Sample preparation materials list

| Code name | A0 | A0.2 | A0.4 | A0.6 | A0.8 | A1 |
|---|---|---|---|---|---|---|
| $H_2O$(g) | 10 | 10 | 10 | 10 | 10 | 10 |
| SA(g） | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| DMAPS(g) | 0 | 0.2 | 0.4 | 0.6 | 0.8 | 1 |
| KPS (wt%) | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $CaCl_2$(%) | 2 | 2 | 2 | 2 | 2 | 2 |
| CNT (wt%) | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| TEMED (uL) | 20 | 20 | 20 | 20 | 20 | 20 |

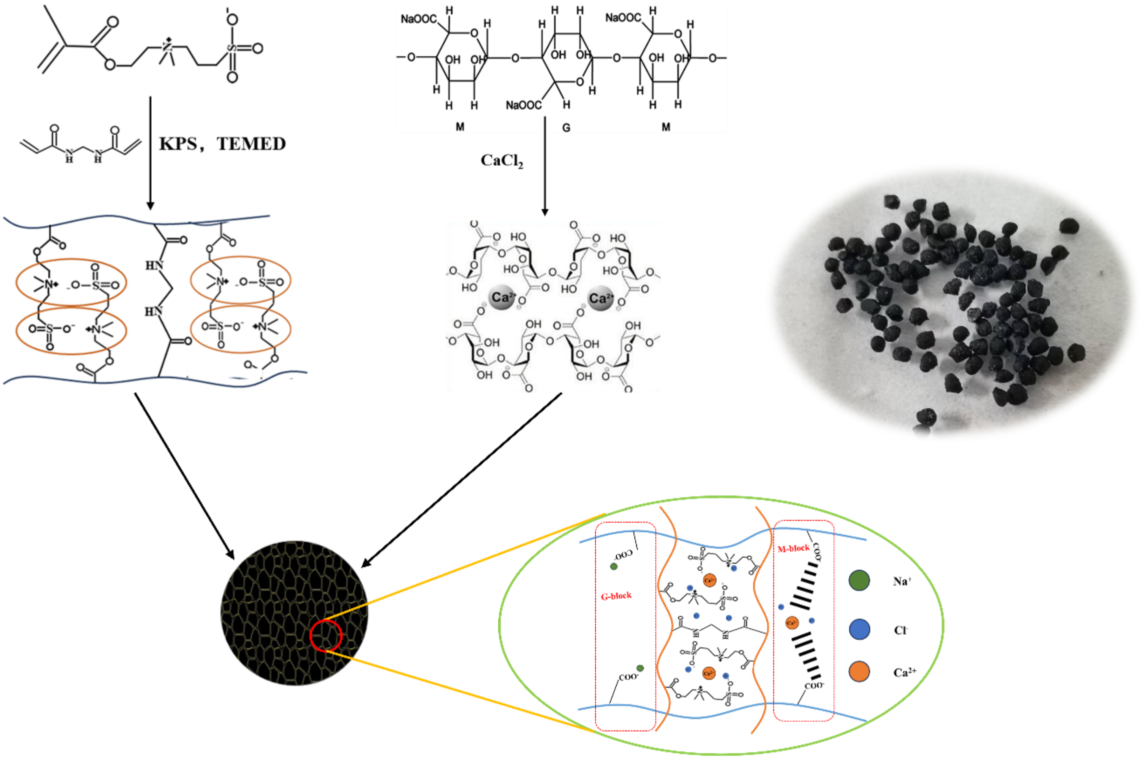


**Figure S1.** Synthesis method and the chemical structure of CA/PDMAPS/CNT/LiCl hydrogel microspheres

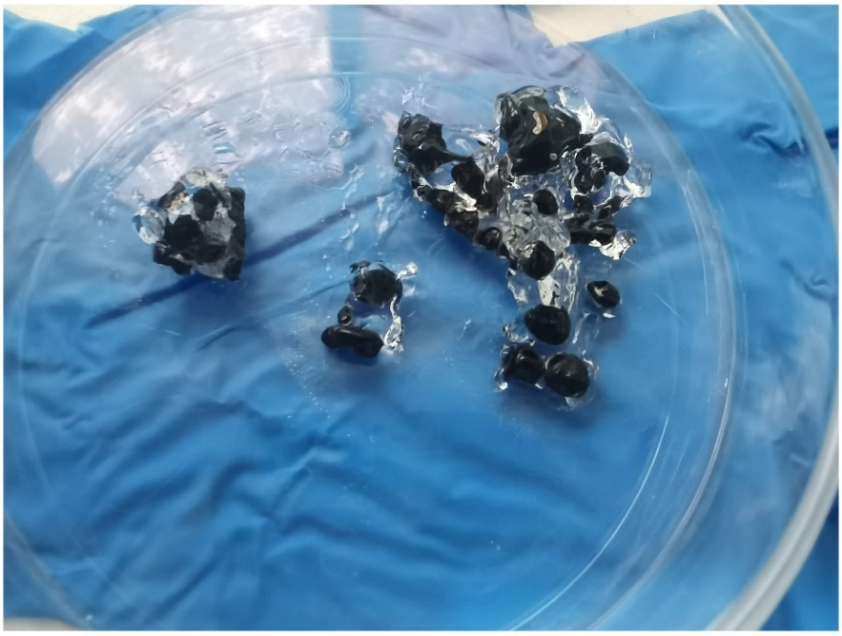


**Figure S2.** Sample picture when the quality ratio of SA: DMAPS is less than 1:6

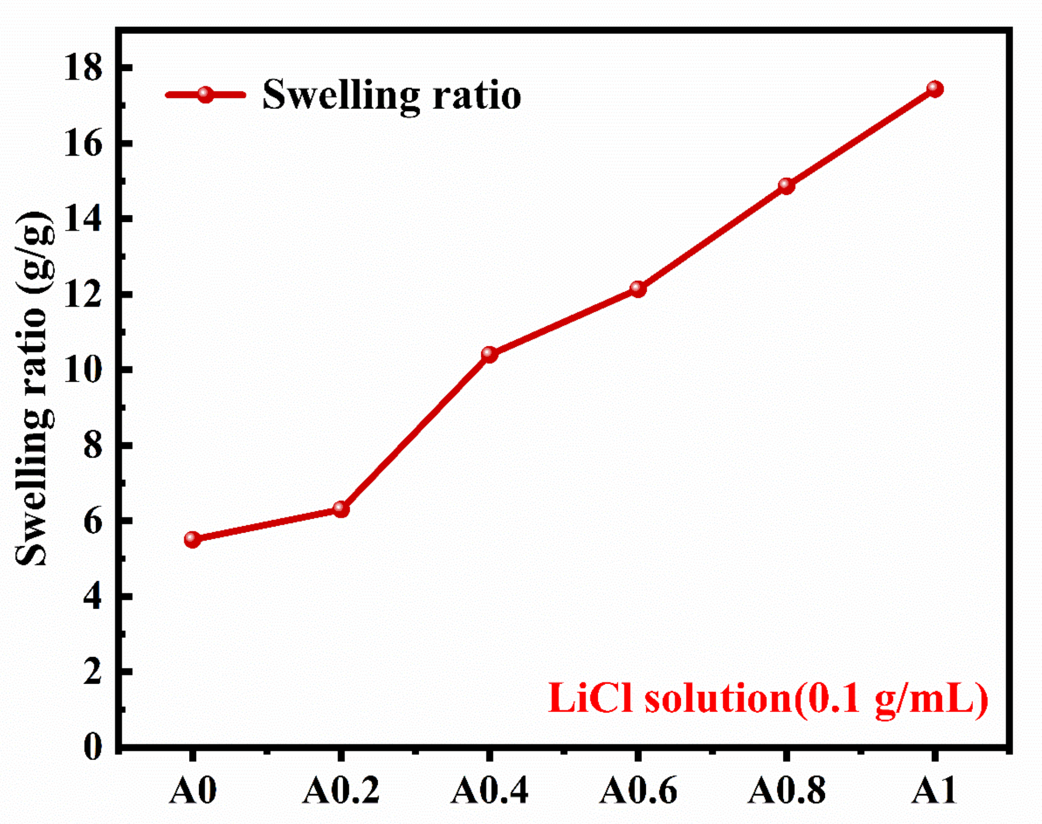


**Figure S3.** Swelling rate of different samples in a 0.1g/mL LiCl solution

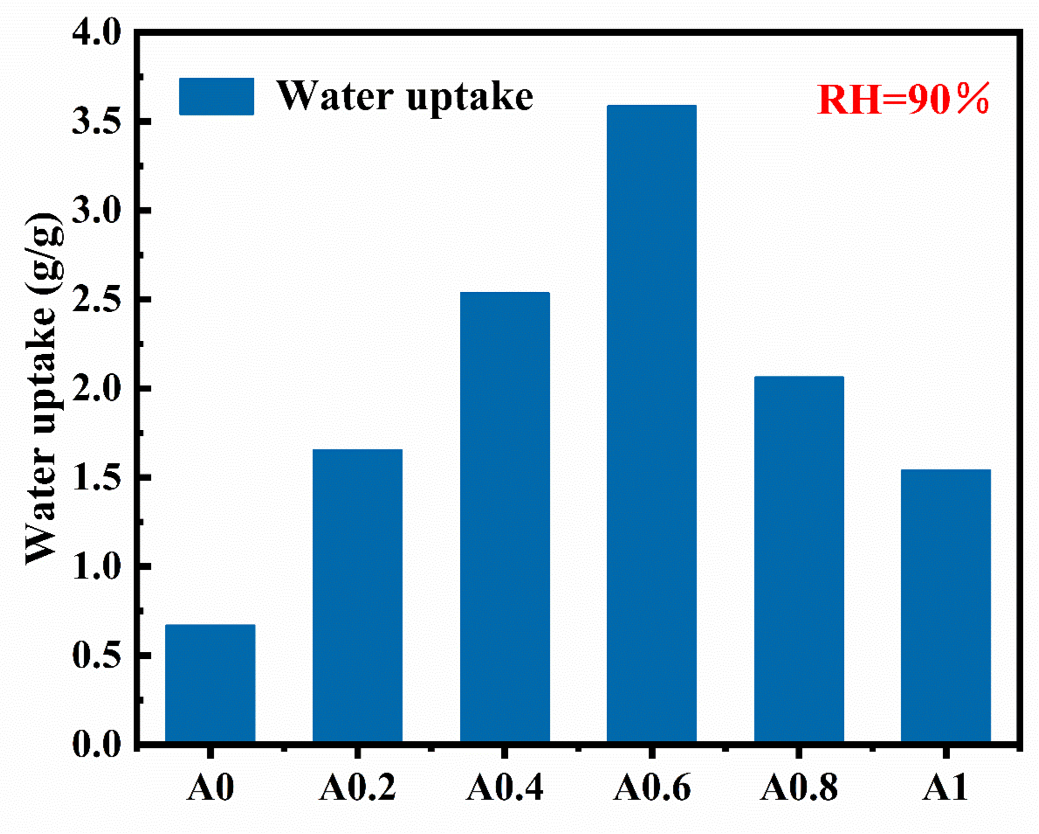


**Figure S4.** Water uptake of different samples at RH= 90%

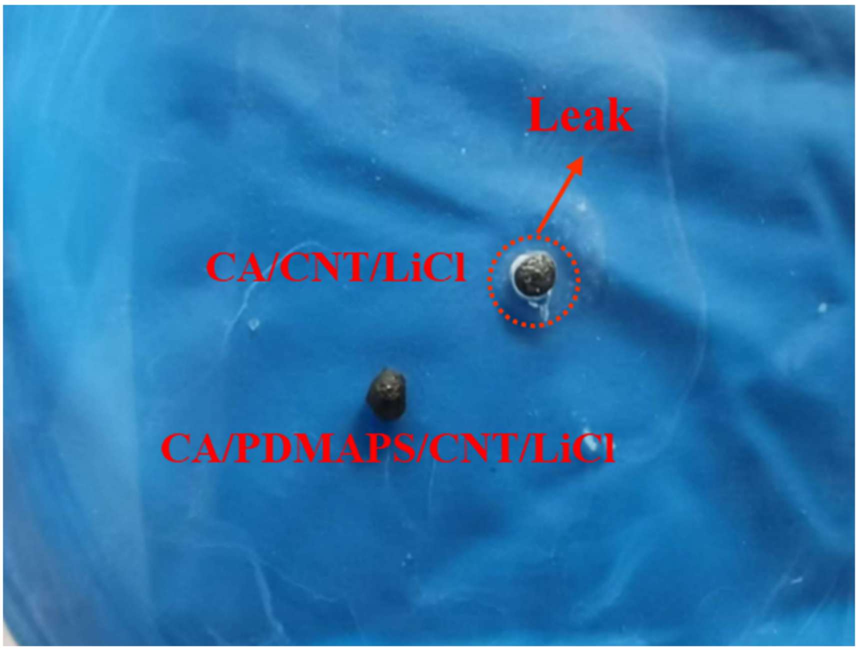
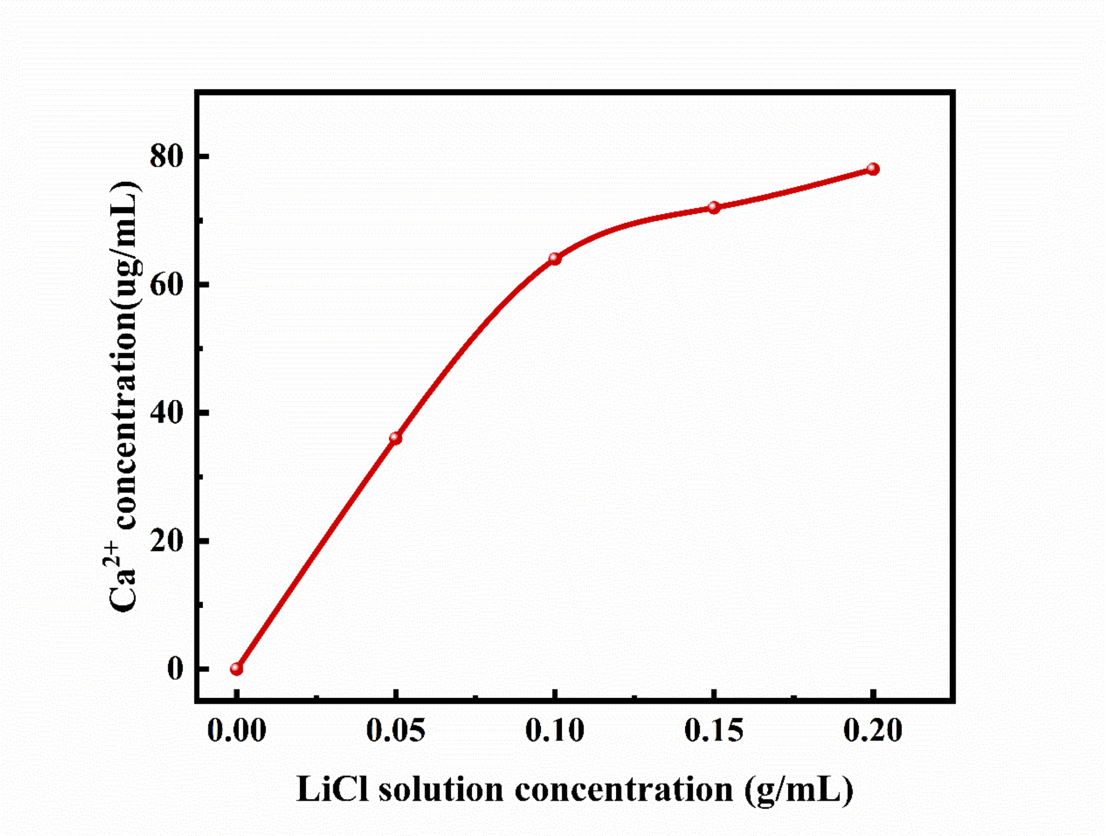


**Figure S5.** CA/CNT/LiCl and CA/PDMAPS/CNT/LiCl hydrogel were loaded with LiCl drying images of the same quality



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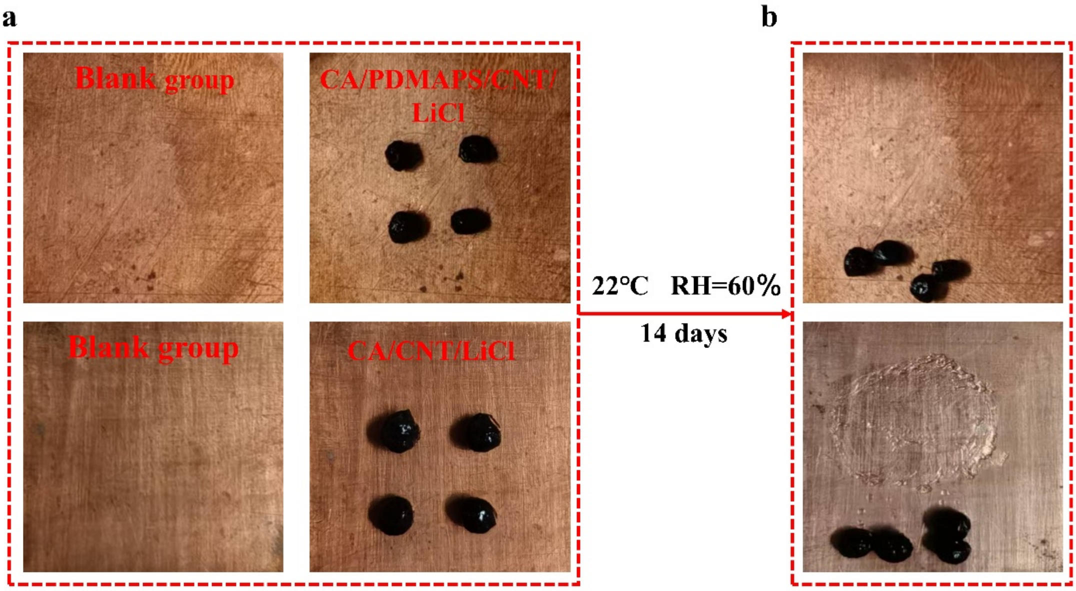

**Figure S7.** LiCl leakage experiment. (a) CA/PDMAPS/CNT/LiCl and CA/CNT/LiCl hydrogels were placed on copper plates and blank groups were set. (b) Copper surface after 14 days at 22°C and RH= 60%.