

# Paper presentation

SCIENCE ADVANCES | RESEARCH ARTICLE

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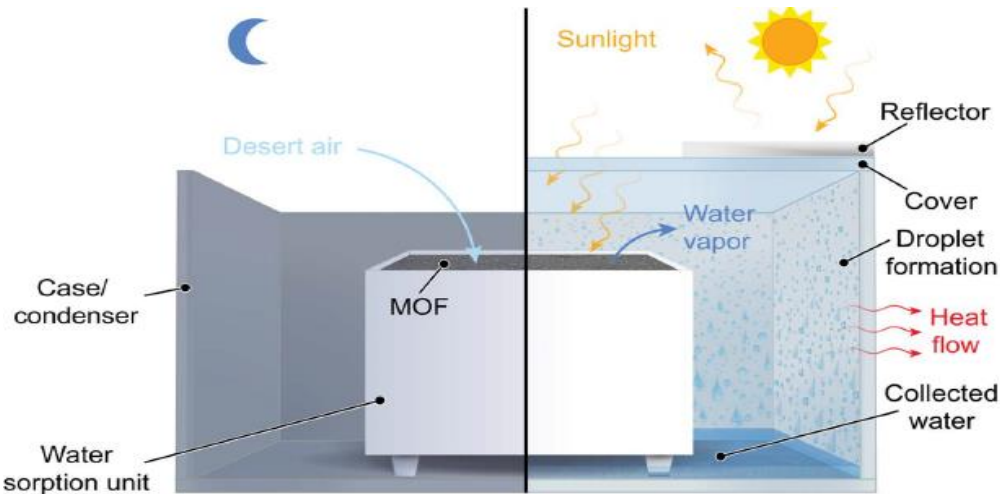
APPLIED SCIENCES AND ENGINEERING

## Autonomous atmospheric water seeping MOF matrix

G. Yilmaz<sup>1</sup>, F. L. Meng<sup>1</sup>, W. Lu<sup>1</sup>, J. Abed<sup>2,3</sup>, C. K. N. Peh<sup>1</sup>, M. Gao<sup>1</sup>, E. H. Sargent<sup>2\*</sup>, G. W. Ho<sup>1,4\*</sup>

Tanmayaa Nayak  
01/05/2021

# BACKGROUND



## COMMUNICATION

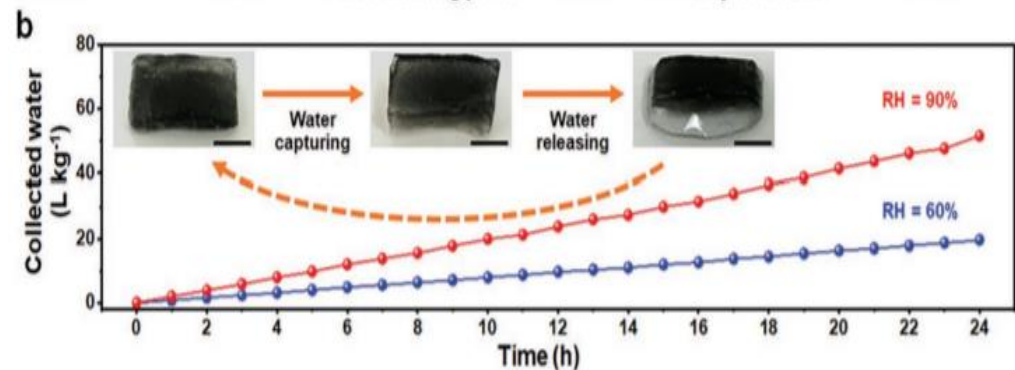
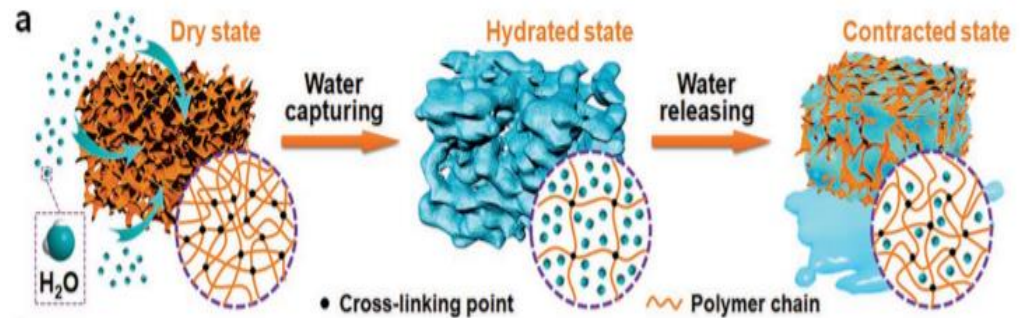
Water Harvesting

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## Super Moisture-Absorbent Gels for All-Weather Atmospheric Water Harvesting

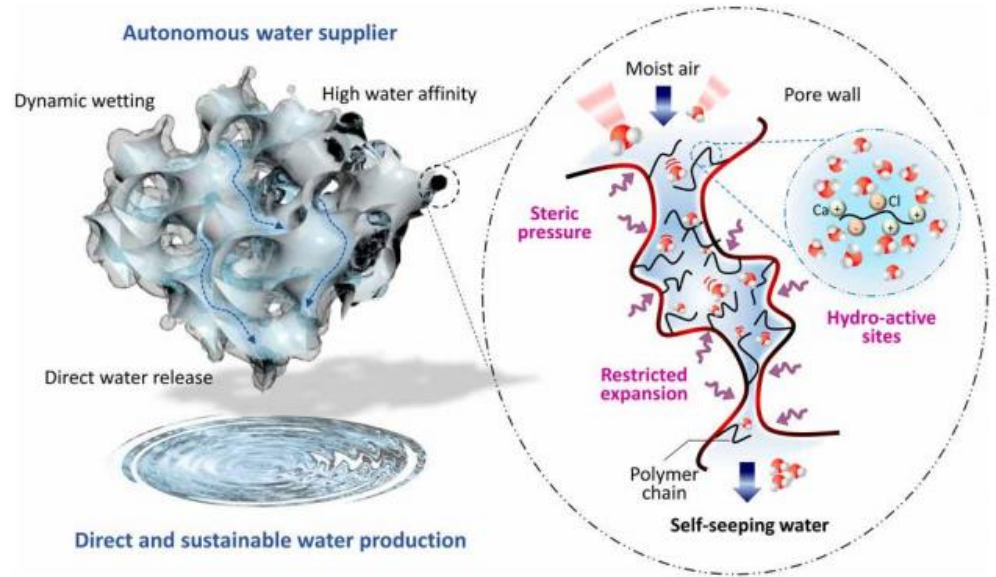
Fei Zhao, Xingyi Zhou, Yi Liu, Ye Shi, Yafei Dai, and Guihua Yu\*

Fathieh et al., Sci. Adv. 2018;4: eaat3198



# INTRODUCTION

- Polymer-MOF (PC-MOF) mixed-matrix materials collect water spontaneously and efficiently at minimum external energy expenditure without ancillary evaporators/condensers
- The tunable hydrophilic chain of the PC-MOF matrix enables them to design for enhanced water uptake and reversible hydrophilic-hydrophobic transitions. These enable autonomous water release and stand-alone airborne water supply without moving parts.
- They reported self-sustained water production that delivers water at  $6.39 \text{ g g}^{-1}$  at 90% RH per day, of which 95% ( $6.04 \text{ g g}^{-1}$ ) leads to direct water collection, and only 5%,  $0.35 \text{ g g}^{-1}$ , is solar desorbed.



Design of the autonomous airborne water supplier. Schematic illustration shows the hydro-active sites on polymer chains that capture atmospheric moisture. Under steric pressure and restricted expansion, the polymer-MOF hybrid pore enables self-seepage for direct water harvesting from ambient.

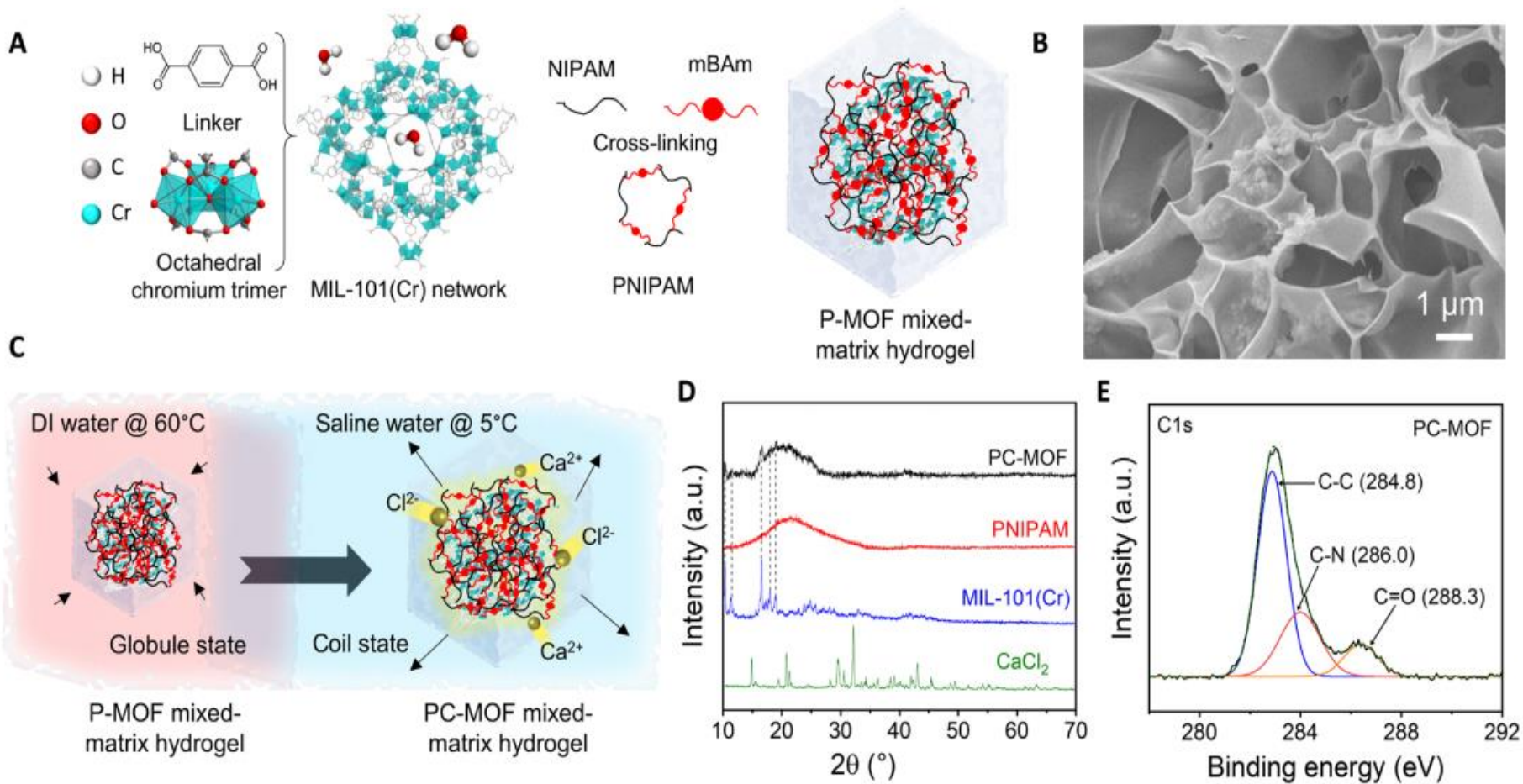
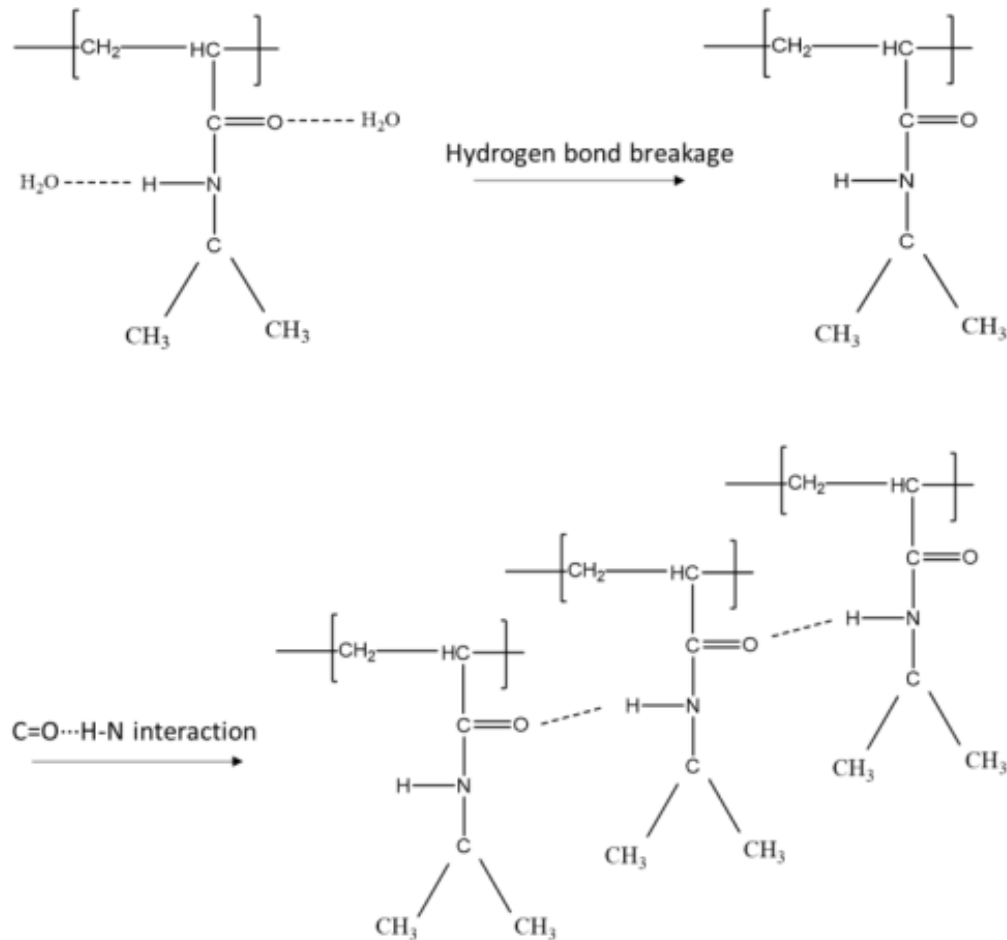


Fig. 2. Fabrication and characterization of the PC-MOF. (A) Units and crystal structure of MIL-101(Cr), schematic cross-linking process of the NIPAM monomer by the mBAm cross-linker, and schematic preparation of the P-MOF mixed-matrix hydrogel. (B) SEM image of the freeze-dried P-MOF mixed-matrix hydrogel. (C) Salinization process of the P-MOF mixed-matrix hydrogel to the PC-MOF mixed-matrix hydrogel. (D) XRD patterns of the MIL-101(Cr), PNIPAM,  $\text{CaCl}_2$ , and PC-MOF. (E) High-resolution C1s XPS spectrum of the PC-MOF. a.u., arbitrary units.



Conformational change in PNIPAM at LCST. Intramolecular hydrogen bond formation ( $\text{C}=\text{O}\cdots\text{H-N}$ ) mechanism. PNIPAM exhibits a phase separation at lower critical solution temperature (LCST), which is accompanied by a structural conformational change. The polymer chain possesses an extended coil conformation below LCST ( $\sim 32^\circ\text{C}$ ) due to hydrogen-bonding interaction of the chains with the water molecules. Above LCST, the long-range interaction between intra-polymer chains are favored ( $\text{C}=\text{O}\cdots\text{H-N}$ ) and short-range hydrogen bonds are broken, resulting in collapse into globular state

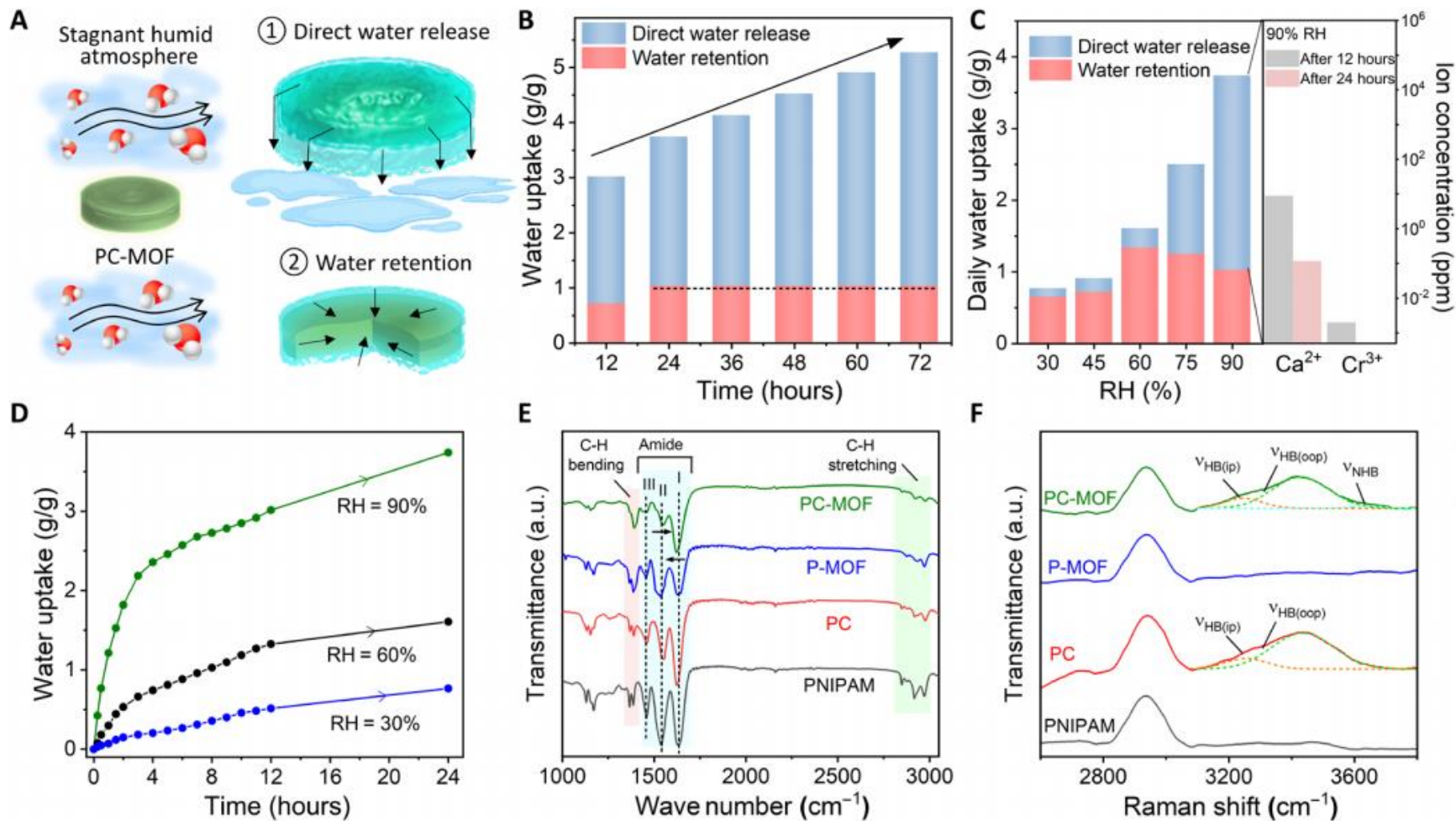


Fig. 3. Atmospheric water uptake and direct release performance of the PC-MOF. (A) Schematic illustration of the water harvesting processes; ① direct water release and ② water retention. (B) Continuous water uptake performance of the PC-MOF for 72 hours at 90% RH. (C) Left: Water uptake mechanism, and performance of the PC-MOF under various RH environments after 24 hours. Right: Measured concentrations of Ca<sup>2+</sup> and Cr<sup>3+</sup> ions in the water collected after 12 and 24 hours of continuous sorption and direct release process at 90% RH. (D) Water uptake rate of the PC-MOF at RHs of 30, 60, and 90%. (E) FTIR spectra of the PNIPAM, PC, P-MOF, and PC-MOF. (F) Raman spectra of the PNIPAM, PC, P-MOF, and PC-MOF after 1-hour adsorption at 90% RH. All moisture sorption experiments were conducted at 25°C.

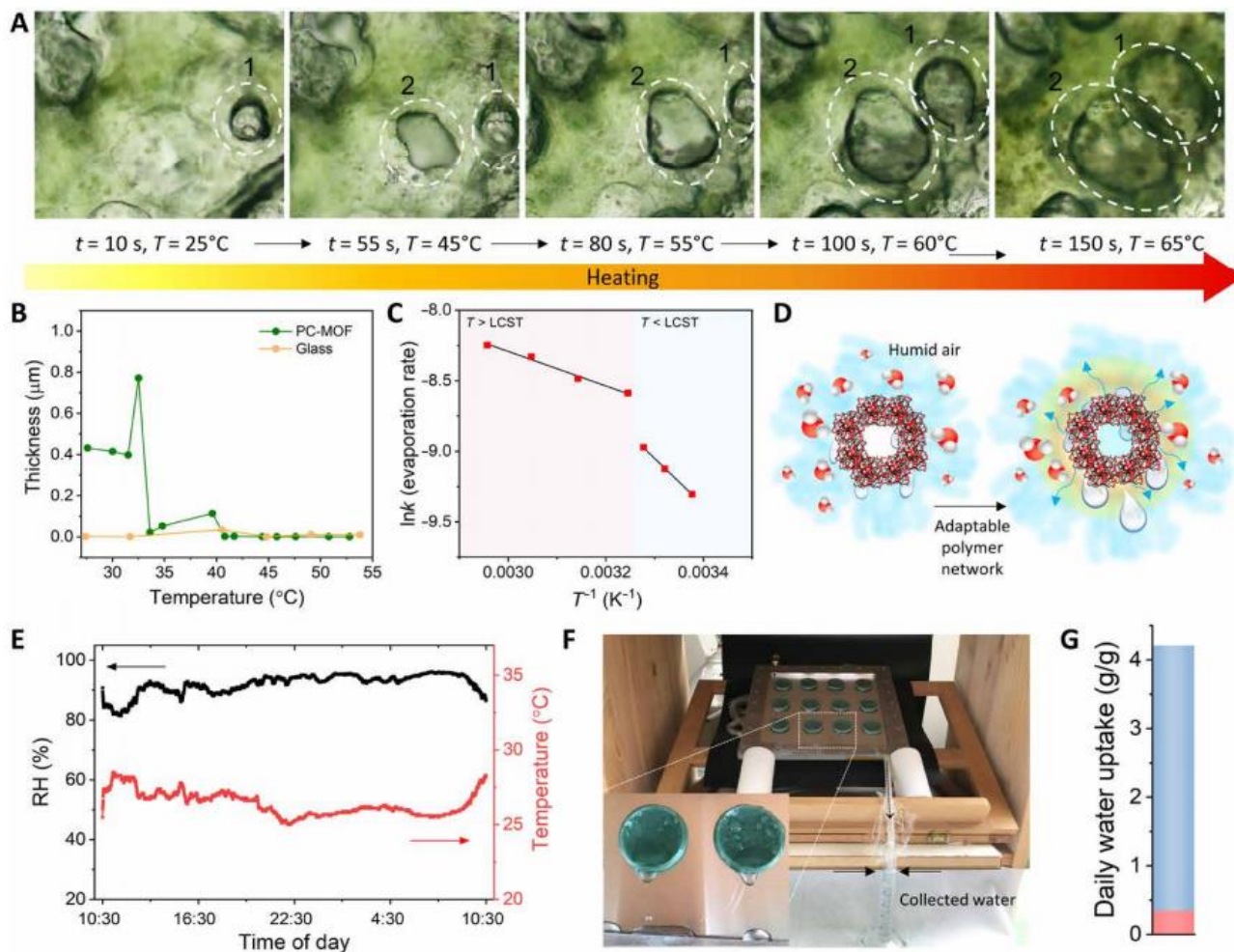


Fig. 4. Optional thermal activation of the PC-MOF for complete water desorption. (A) Optical microscope images demonstrating the temperature-dependent dynamic phase separation behavior of the PC-MOF containing detained water. (B) The thickness of water layer on the PC-MOF surface at various temperatures as determined by the AFM force curve measurements. (C) Arrhenius plot representing the evaporation rate of detained water in PC-MOF as a function of temperature. (D) Schematic illustration of the water evaporation through photothermal effect. (E) The ambient temperature and humidity as functions of time during water harvesting. (F) Photograph of the proof-of-concept prototype for atmospheric water harvesting. (G) Water uptake performance of the PC-MOF; blue and pink portions represent direct water release and water retention, respectively.

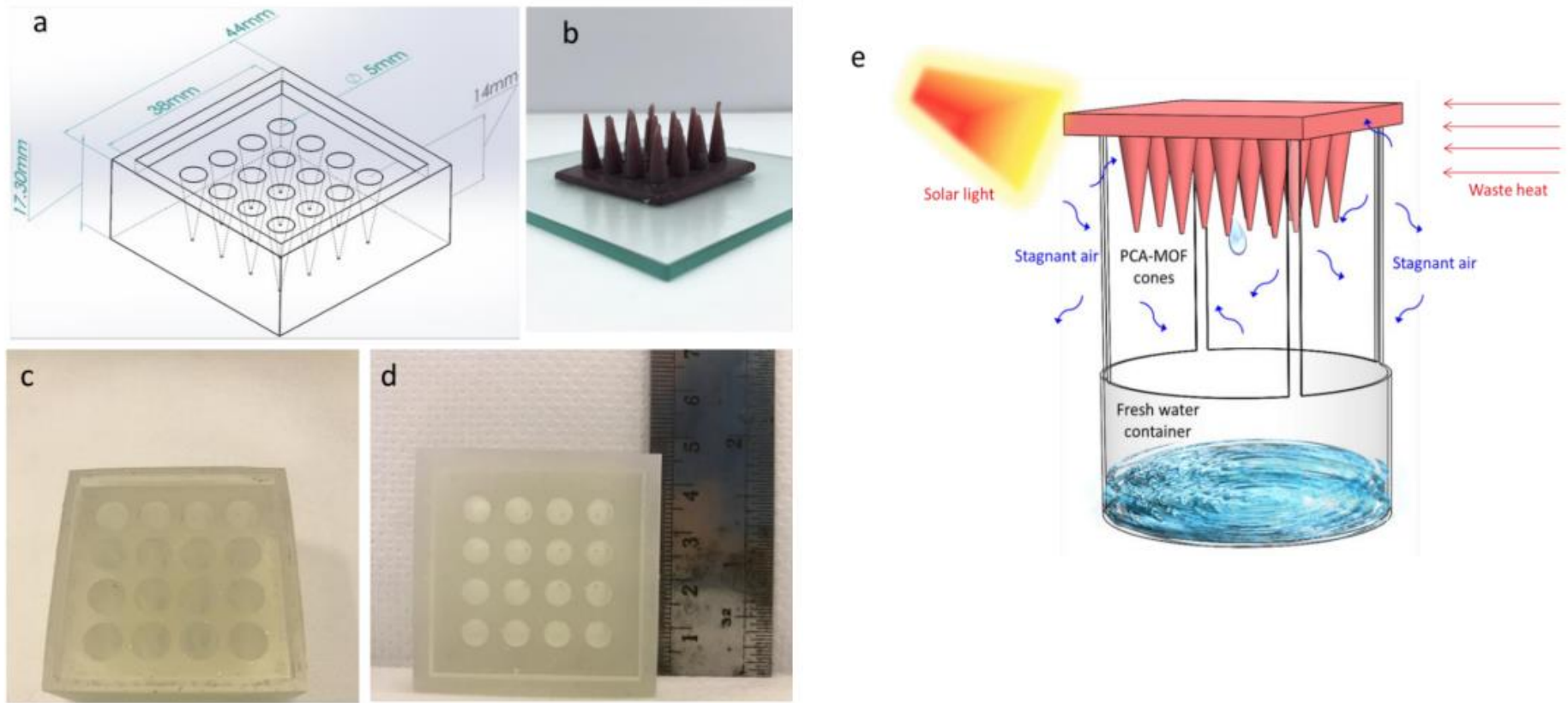
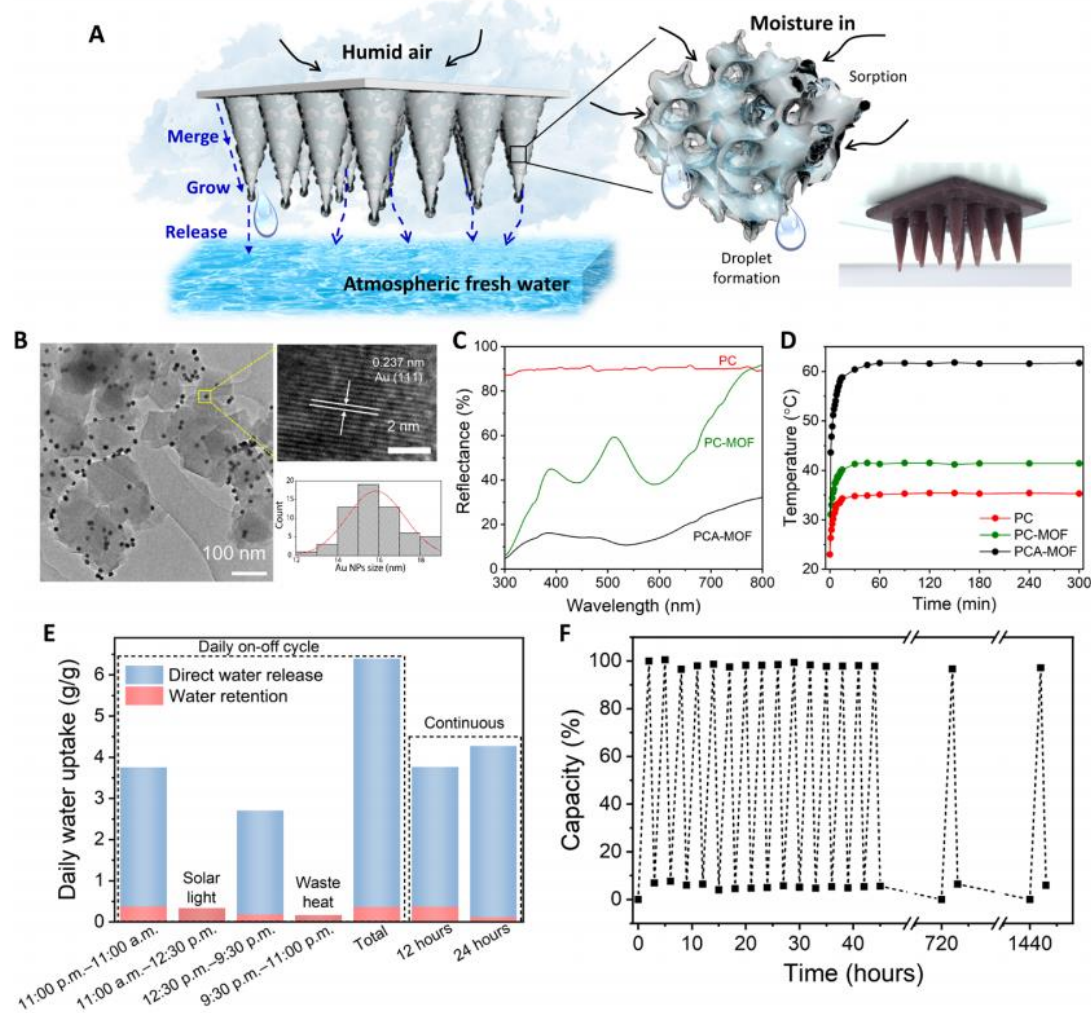


Fig. S25. Preparation of the PCA-MOF cones. (a) 3D drawing of the mold used to prepare PCAMOF cones. (b) Digital image of the PCA-MOF cone structure obtained using the mold. (c), (d) Digital images of the mold. (e) Schematic illustration of the daily water uptake performance of the PCA-MOF cone array via solar-assisted regeneration-based (on-off) for Fig. 5E.





$$\text{Total liquid delivery efficiency (TLDE)}: \frac{\text{amount of liquid delivered}}{\text{amount of sorption}} \quad (1)$$

$$\text{Autonomous liquid delivery efficiency (ALDE)}: \frac{\text{amount of liquid delivered autonomously (no solar input)}}{\text{amount of liquid delivered (optional solar input)}} \quad (2)$$

Fig. 5. Photothermal engineering and structural design. (A) Schematic illustration and digital image of the PCA-MOF cone array. (B) TEM image of the Au@MIL-101(Cr) nanoparticles. The enlarged image shows the HRTEM of Au nanoparticles, and the histogram shows the corresponding size distribution. (C) Reflectance spectra of the PC, PC-MOF, and PCA-MOF. (D) Temperature changes of the PC, PC-MOF, and PCA-MOF over time under 1 sun solar irradiation. (E) Daily on-off cycle: Daily water uptake performance of the PCA-MOF cone array using solar-assisted regeneration. Continuous: Total amount of water uptake after 12 hours (11:00 p.m. to 11:00 a.m.) and 24 hours (11:00 p.m. to 11:00 p.m., next day) without solar-assisted regeneration. (F) Water sorption (2 hours)–release (1 hour) cycles for the PCA-MOF.

# SUMMARY

- Self-sustained atmospheric water harvesting process -polymer-MOF mixed-matrix membrane.
- The cross-linked polymer chain is grafted with hydro-active sites and integrated with a water-stable MOF that serves as a catalyst to accelerate the sorption/desorption kinetics and augment the water uptake. The gel exhibits a remarkable water uptake capability and direct water release property induced through the firm porous water pathways and reduced activation energy.
- **Result**-6.04 g g<sup>-1</sup> liquid water is collected in a day at 90% RH by regenerating the sorbent.

It offers a promising solution for achieving robust, sustainable, and decentralized water production in wideband climatic conditions at minimal energy cost.