Electronic Supplementary Information

LiCl Modified MOFs-Derived Porous Carbon Hollow Spheres for Efficient Solar-driven Atmospheric Water Harvesting

Jiake Jin,[a, b, ϕ] Simiao Guo,[a, b, ϕ] Yue Hu,[a, b] Yefeng Yang,[b, c] Pingwei Ye,[d]* Xinsheng Peng[a, b*]

[a]State Key Laboratory of Silicon and Advanced Semiconductor Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310058, P. R. China

[b]Wenzhou Key Laboratory of Novel Optoelectronic and Nanomaterials, Institute of Wenzhou, Zhejiang University, Wenzhou 325006, P. R. China

E-mail: pengxinsheng@zju.edu.cn

[c]School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, China.

[d]State Key Laboratory of Chemistry for NBC Hazards Protection, Beijing, 102205, P. R. China.

E-mail: yepw2001@163.com

The file includes:

1. **Equation S1-S11.**
2. **Figures S1-S10.**
3. **Tables S1-S5.**

S1. Calculations to evaluate adsorbent performance

To evaluate the water adsorption performance, adsorption-desorption kinetics and other properties of the samples, the following methods are used for calculation in this work.

The water adsorption, desorption and collection capacities ($g \cdot g^{-1}$), the water release ratio (%) and the water collection rate η (%) are used to evaluate the atmospheric water harvesting (AWH) performance of the sorbent.

$$\text{Water adsorption} = (W_1 - W_S) / W_S \quad (1)$$

$$\text{Water desorption} = (W_1 - W_2) / W_S \quad (2)$$

$$\text{Water collection} = W_3 / W_s \quad (3)$$

$$\text{Water adsorption rates} = (W_{t1} - W_S) / (W_S \times t_1) \quad (4)$$

$$\text{Water desorption rates} = (W_1 - W_{t2}) / (W_S \times t_2) \quad (5)$$

$$\text{Water release ratio} = (W_1 - W_2) / (W_1 - W_S) \quad (6)$$

$$\text{Water collection ratio} = \eta = W_3 / (W_1 - W_2) \quad (7)$$

In the formula, W_s (g) is the weight of the dried sample before the experiment. W_1 (g) is the weight of the sample corresponding to the maximum adsorption capacity at a certain moment during the adsorption test. W_2 (g) represents the weight of the sample after desorption for a certain period of time. W_3 (g) indicates the weight of the water collected after desorption and condensation. t_1 (hours, h) is the adsorption time corresponding to the inflection point before the water adsorption reaches equilibrium. In this work, t_1 is selected as approximately 0.833 h, W_{t1} (g) is the weight of the sample corresponding to the moment of t_1. t_2 (h) is the desorption time corresponding to the inflection point before the water desorption reaches equilibrium. In this study, t_2 is selected as approximately 0.833 h; and W_{t2} (g) is the weight of the sample corresponding to the moment of t_2.

In addition, the macro linear driving force model is often used to describe the gas adsorption kinetics, and the formula is as follows:

$$w_t = w_e (1 - e^{-kt}) \quad (8)$$

Among them, w_e ($g \cdot g^{-1}$) is the equilibrium water adsorption capacity of the sorbent; w_t ($g \cdot g^{-1}$) is the dynamic water adsorption capacity of the adsorbent at time *t*. *k* (min^{-1}) represents the adsorption rate constant, which depends on the particle size of the adsorbent, the gas diffusion situation, etc. *t* (min) represents the time.

The performance of LiCl loaded in the sample sorbent is also calculated, and the relevant

formulas are as follows:

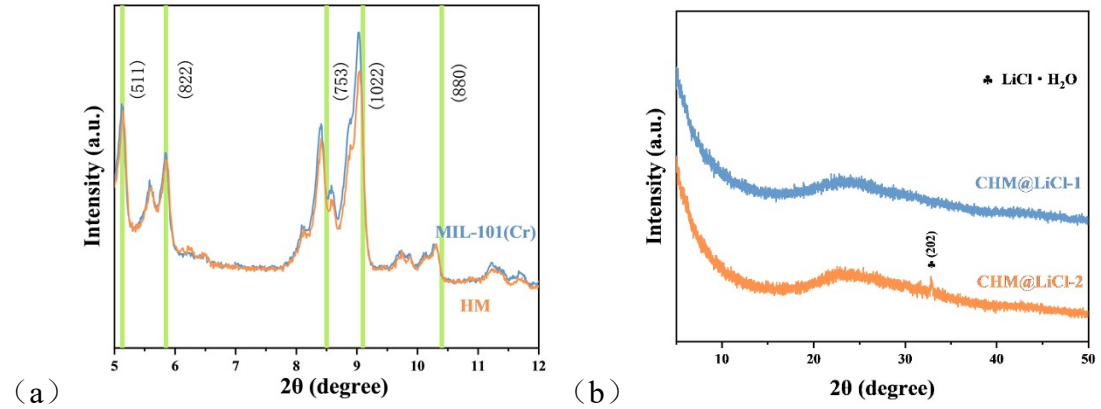
$$\text{Water adsorption} = Q = (Q_{sorbent} - Q_{sorbent\text{-}w} \times C_{sorbent\text{-}w}) / C_{LiCl} \quad (9)$$

$$\text{Water adsorption rates} = Q_{t1} / t_1 \quad (10)$$

$$\text{Water desorption rates} = (Q_m - Q_{t2}) / t_2 \quad (11)$$

Among them, $Q_{sorbent}$ ($g \cdot g^{-1}$) is the water adsorption capacity of the sample. $Q_{sorbent\text{-}w}$ ($g \cdot g^{-1}$) is the water adsorption capacity of sorbent-w. C_{LiCl} (wt.%) represents the mass percentage of LiCl loaded in the sample. $C_{sorbent\text{-}w}$ represents the mass percentage of the porous carbon after removing LiCl (where $C_{sorbent\text{-}w} + C_{LiCl} = 1$). Q_{t1} ($g \cdot g^{-1}$) is the water adsorption capacity of LiCl in the prepared sorbents corresponding to the moment of t_1. Q_m ($g \cdot g^{-1}$) is the water adsorption capacity of LiCl in the prepared adsorbent when the water adsorption reaches equilibrium. Q_{t2} ($g \cdot g^{-1}$) is the water adsorption capacity of LiCl in the prepared sorbents corresponding to the moment of t_2.

S2. Supporting Figures and Tables



（a） （b）

Fig. S1 (a) low-angle XRD patterns of MIL-101(Cr). (b) XRD patterns of CHM@LiCl-1 and CHM@LiCl-2.

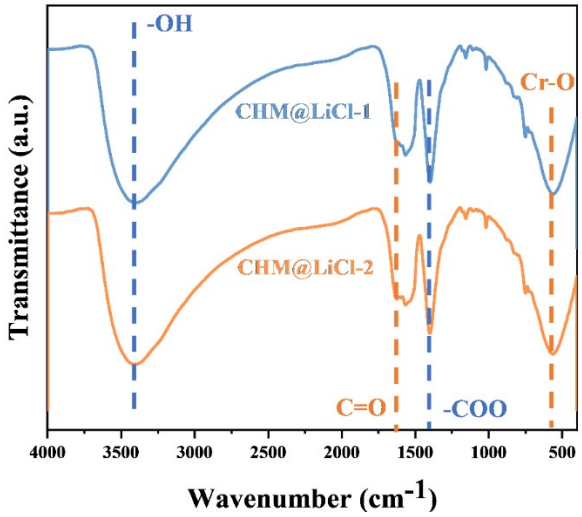


Fig. S2 FTIR spectra of CHM@LiCl-1 and CHM@LiCl-2.

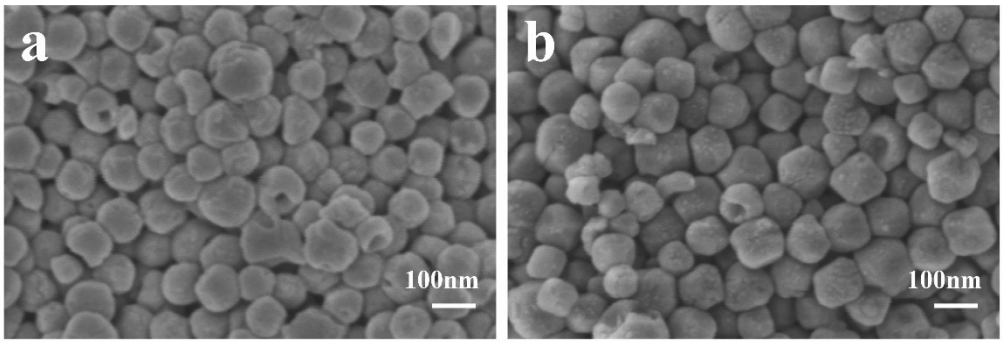


Fig. S3 SEM images of (a) CHM@LiCl-1, (b) CHM@LiCl-2.

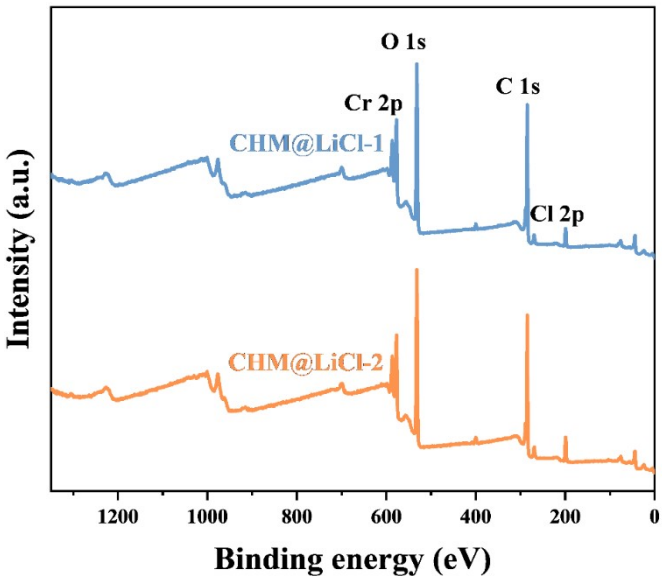


Fig. S4 XPS spectra of CHM@LiCl-1 and CHM@LiCl-2.

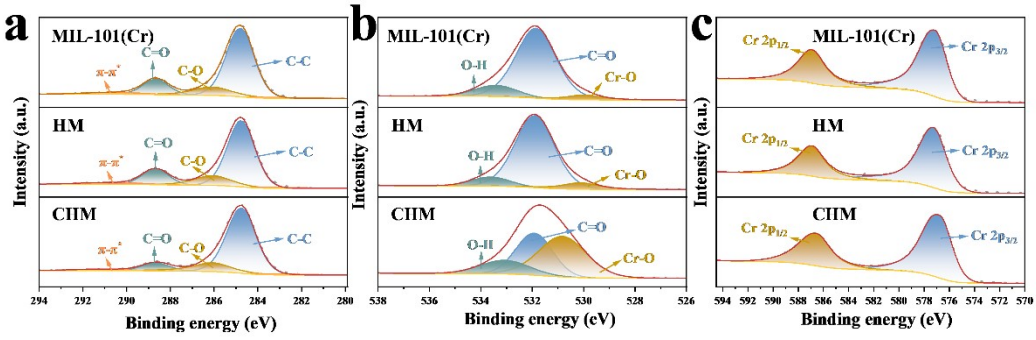


Fig. S5 High-resolution XPS (a) C 1s spectra. (b) O 1s spectra. (c) Cr 2p spectra of MIL-101(Cr), HM and CHM respectively.

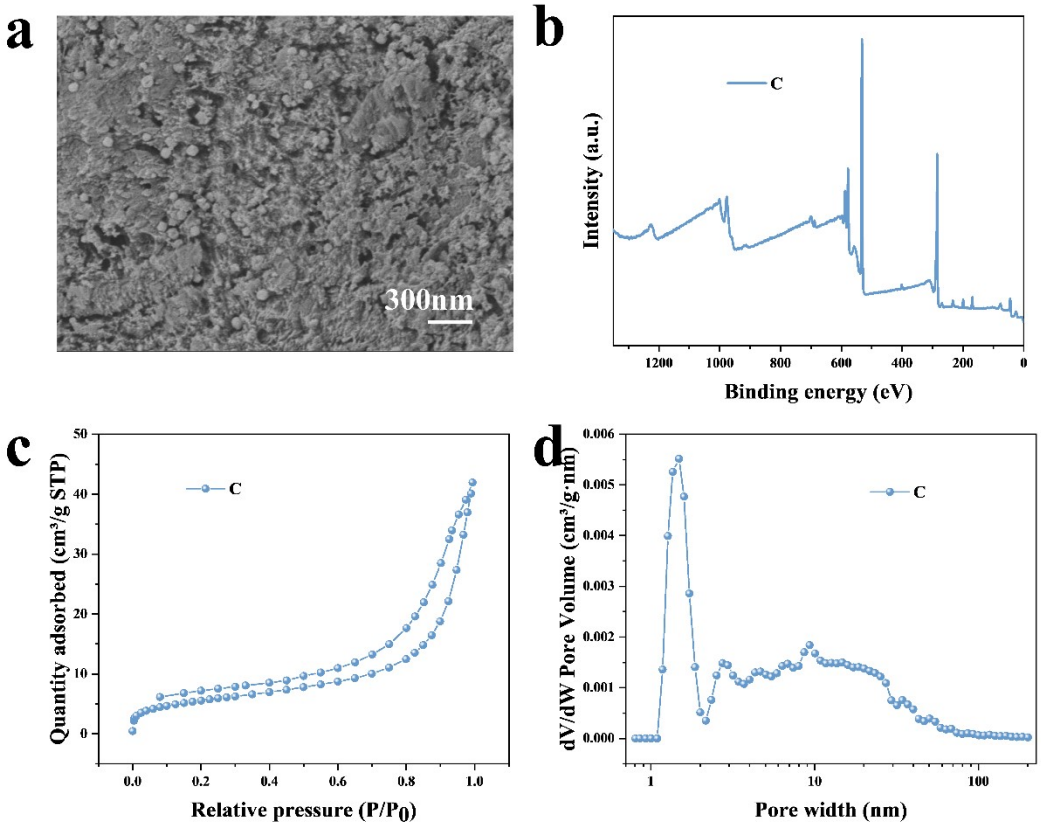


Fig. S6 (a) SEM images, (b) XPS spectra, (c) The N2 adsorption-desorption isotherms and (d) Pore size distribution curves of C sample without Chromium oxides.

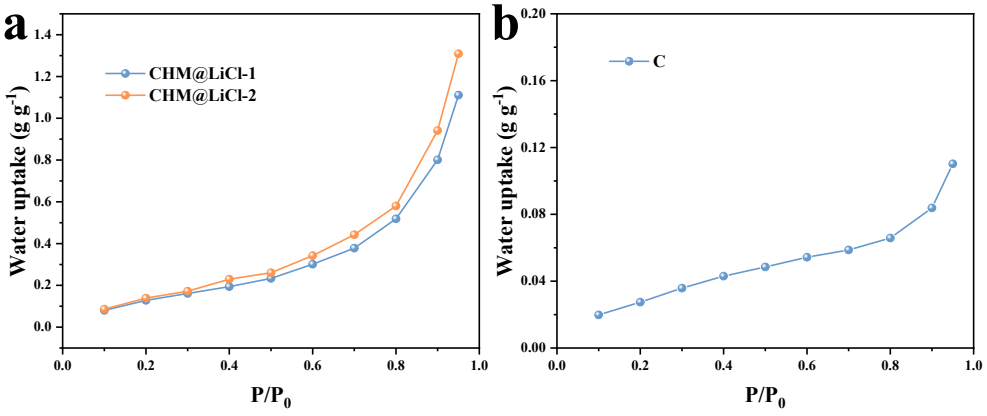


Fig. S7 (a) Water vapor sorption isotherms of CHM@LiCl-1 and CHM@LiCl-2. (b) Water vapor sorption isotherms of C sample without Chromium oxides.

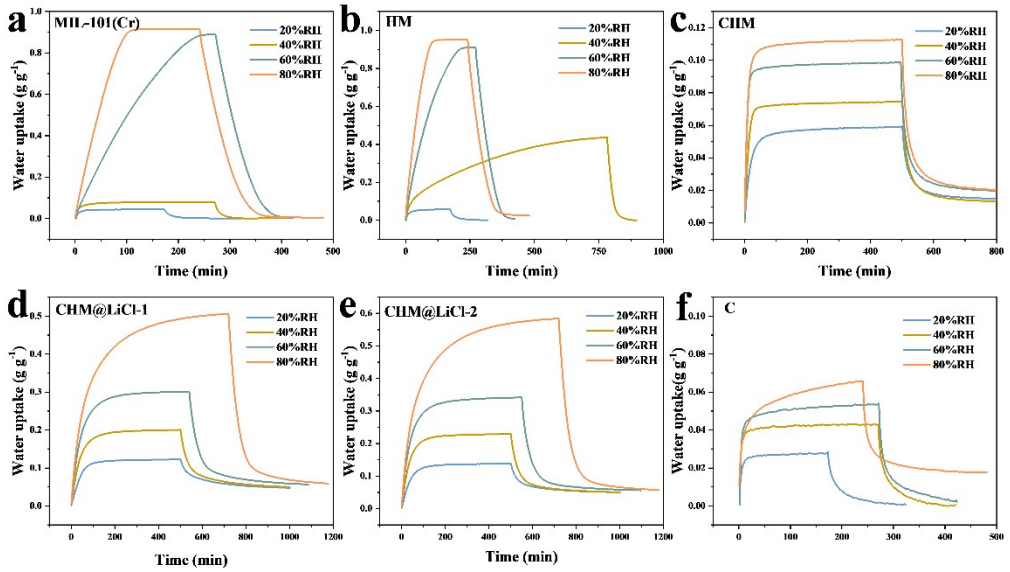


Fig. S8 The static water sorption curves at 20~80% RH for (a) MIL-101(Cr), (b) HM, (c) CHM, (d) CHM@LiCl-1, (e) CHM@LiCl-2 and (f) C sample without Chromium oxides, respectively.

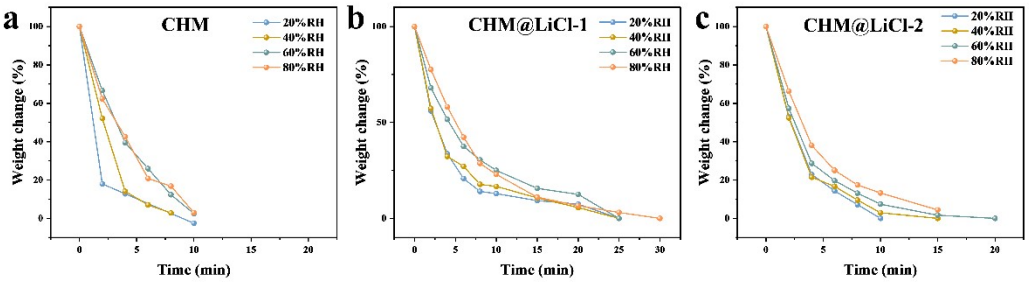


Fig. S9 Weight change curves of sorbents under simulated sunlight for (a) CHM, (b) CHM@LiCl-1 and (c) CHM@LiCl-2, respectively.

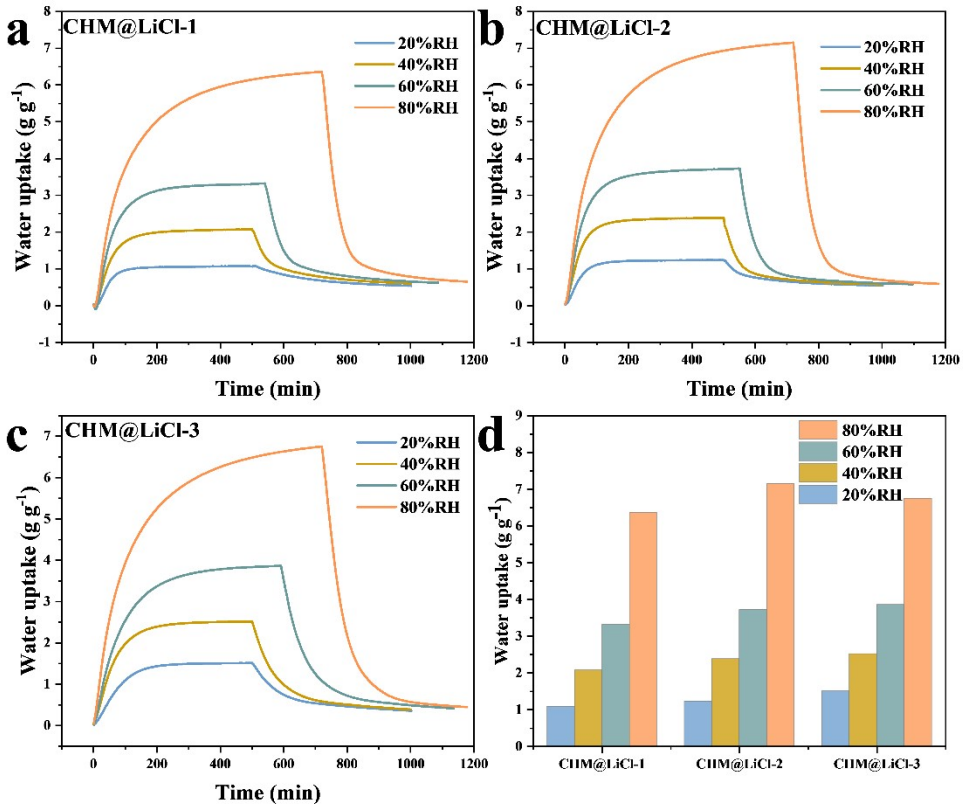


Fig. S10 The static water sorption curves at 20~80% RH for (a) LiCl in CHM@LiCl-1, (b) LiCl in CHM@LiCl-2, (c) LiCl in CHM@LiCl-3. (d) The water uptake of LiCl in different CHM@LiCl sorbents.

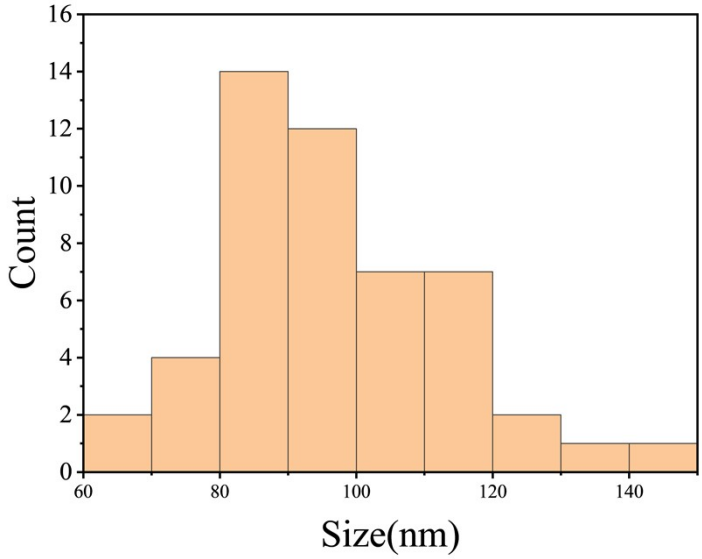


Fig. S11 Histogram of Size Statistics for HM.

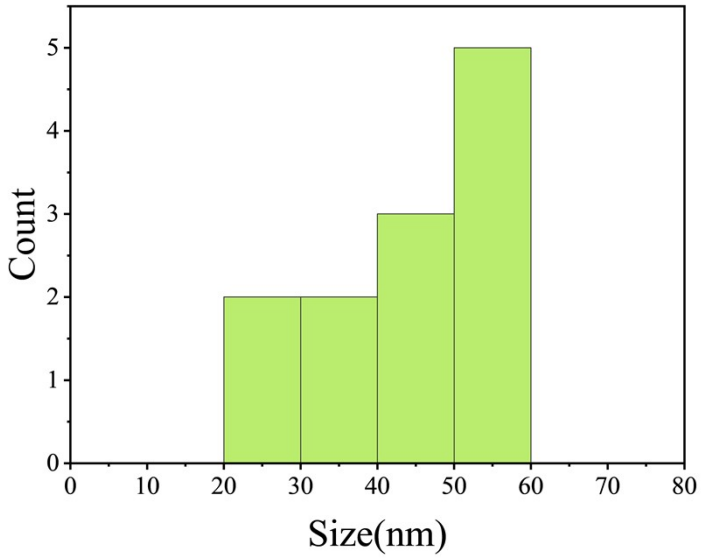


Fig. S12 Histogram of Size Statistics for cavity of HM.

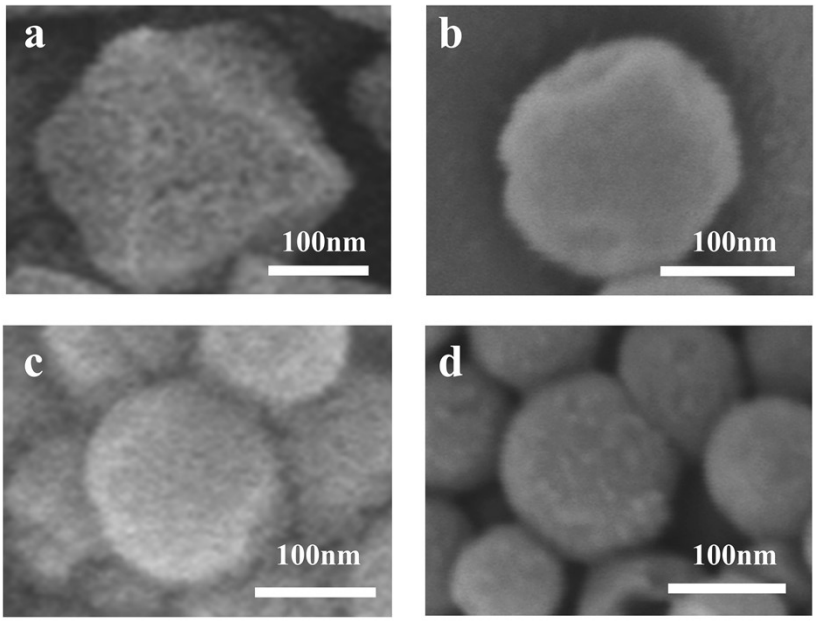


Fig. S13 SEM images of (a) MIL-101(Cr), (b) HM, (c) CHM and (d) CHM@LiCl-3.

Table S1 The amount of LiCl in CHM@LiCl sorbents

Samples	LiCl loading（wt.%）
CHM@LiCl-1	6.3
CHM@LiCl-2	6.7
CHM@LiCl-3	13.4

Table S2 BET and pore volume of different samples

Samples	BET（m^2/g）	Pore volume（cm^3/g）
MIL-101(Cr)	2,644.21	1.58
HM	2,802.64	1.63
CHM	327.49	0.33
CHM@LiCl-3	44.16	0.14
C	20.21	0.06

Table S3 w_e of the sorbents at different humidity levels

Samples	20% RH	40% RH	60% RH	80% RH
CHM	0.058	0.074	0.097	0.11
CHM@LiCl-1	0.12	0.20	0.30	0.49
CHM@LiCl-2	0.14	0.23	0.34	0.57
CHM@LiCl-3	0.26	0.40	0.60	0.97

Table S4 k of the sorbents at different humidity levels

Samples	20%RH	40%RH	60%RH	80%RH
CHM	0.046	0.082	0.12	0.097
CHM@LiCl-1	0.024	0.024	0.020	0.011
CHM@LiCl-2	0.025	0.027	0.023	0.012
CHM@LiCl-3	0.014	0.017	0.013	0.010

Table S5. Comparison of the water sorption performance for the sorbents in this work and previous publications

Materials	Loaded LiCl (wt.%)	Temperature (°C)	Relative humidity (%)	Water uptake (g g^{-1})	LiCl water uptake (g g^{-1})	Ref.
LiCl@rGO-SA	78	30	15	1.01	1.29	[1]
LiCl@rGO-SA	78	30	30	1.52	1.95	[1]
LiCl@rGO-SA	78	30	60	2.76	3.54	[1]
LiCl@PCP	46	25	15	0.43	0.93	[2]
LiCl@PCP	46	25	30	0.89	1.93	[2]
LiCl@PCP	46	25	60	1.48	3.22	[2]
LiCl@MIL-101(Cr)	51	30	30	0.77	1.51	[3]
LiCl@PAM	68	25	20	1.1	1.62	[4]
LiCl@PAM	68	25	30	1.5	2.21	[4]
LiCl@SA-MXene	68.4	25	45	1.86	2.72	[5]
LiCl@HMS-PPy	30.39	25	30	0.784	2.58	[6]
LiCl@HMS-PPy	30.39	25	60	1.396	4.59	[6]
LiCl@HMS-PPy	30.39	25	80	2.012	6.62	[6]
LiCl@CNF-CNT	60	25	11	0.33	0.55	[7]
LiCl@CNF-CNT	60	25	33	0.73	1.22	[7]
LiCl@CNF-CNT	60	25	57	1.15	1.92	[7]
LiCl@CNF-CNT	60	25	75	1.48	2.47	[7]
LiCl@CNF-CNT	60	25	95	1.59	2.65	[7]
this work	**13.4**	**25**	**20**	**0.25**	**1.87**	
this work	**13.4**	**25**	**30**	**0.31**	**2.31**	
this work	**13.4**	**25**	**40**	**0.39**	**2.91**	
this work	**13.4**	**25**	**60**	**0.6**	**4.48**	
this work	**13.4**	**25**	**80**	**1.04**	**7.76**	

References

1. J. Xu, T. Li, T. Yan, S. Wu, M. Wu, J. Chao, X. Huo, P. Wang and R. Wang, *Energy Environ. Sci.*, 2021, **14**, 5979-5994.

2. J. Wang, W. Ying, B. Lin, C. Li, C. Deng, H. Zhang, S. Wang and R. Wang, *Adv. Mater.*, 2025, **37**, 2408977.

3. J. Xu, T. Li, J. Chao, S. Wu, T. Yan, W. Li, B. Cao and R. Wang, *Angew. Chem. Int. Ed.*, 2020, **59**, 5202-5210.

4. H. Lu, W. Shi, J. H. Zhang, A. C. Chen, W. Guan, C. Lei, J. R. Greer, S. V. Boriskina and G. Yu, *Adv. Mater.*, 2022, **34**, e2205344.

5. J. Chen, M. Zhu, G. He, H. Yang, Z. Deng, J. Du, X. Liu, J. Huang, S. Gu and B. Shang, *Desalination*, 2025, **595**, 118319.

6. X. Han, L. Zhong, L. Zhang, L. Zhu, M. Zhou, S. Wang, D. Yu, H. Chen, Y. Hou and Y. Zheng, *Small*, 2023, **19**, 2303358.

7. P. Zhu, Z. Yu, H. Sun, D. Zheng, Y. Zheng, Y. Qian, Y. Wei, J. Lee, S. Srebnik, W. Chen, G. Chen and F. Jiang, *Adv. Mater.*, 2024, **36**, e2306653.