Supplementary Information

MOFs supraparticles for atmosphere water harvesting at low humidity

Yue Hu,^a Yuqi Wang,^a Zhou Fang,^a Xinyi Wan,^a Mengyang Dong,^a Zhizhen Ye,^{a, b}

Xinsheng Peng^{a, b}*

^aState Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China ^bWenzhou Key Laboratory of Novel Optoelectronic and Nanomaterials, Institute of Wenzhou, Zhejiang University, Wenzhou 325006, P. R. China E-mail: <u>pengxinsheng@zju.edu.cn</u>

The file includes:

1. The preparation of MIL-101-PVP (Note S1).

2. The calculation process of the water uptake of single MOF in M-8010 supraparticles (Note S2).

3. Additional figures and tables.

1. The preparation of MIL-101-PVP (Note S1).

MIL-101(Cr) (40 mg) and PVP (120 mg) were ultrasonically dispersed in 20 ml of DMF solution, followed by magnetic stirring for 12 hours, to obtain a homogeneous suspension, and then reacted in an oil bath at 130 °C for 20 minutes (1500 rpm), followed by centrifugation and the removal of supernatant. Subsequently, the products were re-dispersed in 20 mL of DMF solution, and then reacted in an oil bath at 130 °C for 80 minutes to obtain MIL-101-PVP. The final product was centrifuged (10000 rpm, 10 min) and washed by DMF and methanol, three times respectively, and then dried at 80 °C for 12 hours.

2. The calculation process of the water uptake of single MOF in M-8010 supraparticles. (Note S2)

 $m_{MOF\text{-}801}/\ m_{MIL\text{-}101}\,{=}\,45.44$ wt.% / 54.56 wt.%

If the mass of M-8010 supraparticles is m (g), the water uptake at specific relative pressure of M-8010 supraparticles, pure MOF-801, pure MIL-101 is Q_0 (g/g), Q_1 (g/g), Q_2 (g/g), respectively,

Then

 $m_{MOF-801} = 0.4544 m (g), m_{MIL-101} = 0.5456 m (g)$

Assuming that the water adsorption capacity at specific relative pressure of MIL-

101 in M-8010 is unchanged, then the water uptake at specific relative pressure of MOF-801 in M-8010 can be calculated as Q_3 ,

$$Q_3 = (Q_0 - Q_2 * m_{MIL-101}) / m_{MOF-801} (g/g)$$

Assuming that the water adsorption capacity at specific relative pressure of MOF-

801 in M-8010 is unchanged, then the water uptake at specific relative pressure of MIL-

101 in M-8010 can be calculated as Q₄,

$$Q_4 = (Q_0 - Q_1 * m_{MOF-801}) / m_{MIL-101} (g/g)$$

3. Additional figures and tables.



Figure S1. (a) UV-vis-NIR spectra of MOF-801, MIL-101 and M-8010. (b) TGA curves of MOF-801, MIL-101, M-8010 and PVP (from 50 °C to 800 °C).



Figure S2. TEM and EDX elemental mapping images of MOF-801, scar bar is 200 nm.



Figure S3. TEM and EDX elemental mapping images of MIL-101, scar bar is 500 nm.



Figure S4. TEM and EDX elemental mapping images of M-8010, scar bar is 500 nm.



Figure S5. SEM image of physical mixture of MOF-801 and MIL-101 without PVP.



Figure S6. SEM image of MOF-801@MIL-101 particles without secondary nucleation and self-assembled growth.



Figure S7. SEM image of MOF-801@MIL-101 particles obtained with excess reaction time.



Figure S8. The water vapor adsorption isotherms of (a) polyvinylpyrrolidone (PVP) and (b) MIL-101-PVP.



Figure S9. Water vapor adsorption isotherms of MOF-801, MIL-101 and M-8010.



Figure S10. The water vapor adsorption isotherm of the physical mixture of MOF-801 and MIL-101 with a mass ratio of 1:1.



Figure S11. Water adsorption isotherm of M-8010 at 40 °C and corresponding isotherms adsorption heat curve of M-8010 supraparticles.



Figure S12. N_2 adsorption isotherms and pore size distribution curves of MOF-801, MIL-101 and M-8010.

Sample	BET Surface Area	Pore Volume	
	m²/g	cm ³ /g	
MOF-801	610	0.41	
MIL-101	2485.5	1.34	
M-8010	928.2	0.76	

Table S1. Details of BET surface area and pore volume of MOF-801, MIL-101 and M-8010.



Figure S13. Fitting curves of water uptake over time of MOF-801, MIL-101 and M-8010 at 10% RH (25 °C).

Table S2. The results about the fitting curves (Figure S12) of water uptake over time of MOF-801, MIL-101 and M-8010 at 10% RH (25 °C).

Model	BoxLucas1		
Equaption	$y = a^{*}(1 - exp(-b^{*}x))$		
Sample	MOF-801	MIL-101	M-8010
a	0.09943 ± 0.0025	0.03194 ± 3.72073E-4	0.16653 ± 0.0053
b	0.07608 ± 0.00774	0.24723 ± 0.02364	0.03985 ± 0.00383
Reduced Chi-Sqr	3.80067E-5	1.43709E-6	1.0707E-4
R-Square(COD)	0.95851	0.9822	0.96209
Adj. R-Square	0.95506	0.98072	0.95893



Figure S14. Fitting curves of water uptake over time of MOF-801, MIL-101 and M-8010 at 15% RH (25 °C).

Table S3. The results about the fitting curves of water uptake over time of MOF-801, MIL-101 and M-8010 at 15% RH (25 °C).

Model	BoxLucas1		
Equaption	$y = a^{*}(1 - exp(-b^{*}x))$		
Sample	MOF-801	MIL-101	M-8010
a	0.19468 ± 0.00289	0.03986 ± 2.67287E-4	0.20558 ± 0.00434
b	0.03161 ± 0.0013	0.1832 ± 0.00825	0.03836 ± 0.00241
Reduced Chi-Sqr	2.55102E-5	6.74572E-7	6.93941E-5
R-Square(COD)	0.99399	0.9948	0.98477
Adj. R-Square	0.99349	0.99437	0.9835



Figure S15. Fitting curves of water uptake over time of MOF-801, MIL-101 and M-8010 at 20% RH (25 °C).

Table S4. The results about the fitting curves of water uptake over time of MOF-801, MIL-101 and M-8010 at 20% RH (25 °C).

Model	BoxLucas1		
Equaption	$y = a^{*}(1 - exp(-b^{*}x))$		
Sample	MOF-801	MIL-101	M-8010
a	0.2326 ± 0.00153	0.04299 ± 2.61672E-4	0.23699 ± 0.00164
b	0.06002 ± 0.00142	0.25249 ± 0.01281	0.0458 ± 0.00101
Reduced Chi-Sqr	1.21814E-5	7.14679E-7	1.15769E-5
R-Square(COD)	0.99785	0.9951	0.99813
Adj. R-Square	0.99767	0.9947	0.99797



Figure S16. Time-dependent temperature change curves of M-8010 supraparticles under different light intensities $(0.1 \text{ W/cm}^2, 0.2 \text{ W/cm}^2, 0.4 \text{ W/cm}^2 \text{ and } 0.6 \text{ W/cm}^2)$. (In the first 600 s, the light was turned on; in the last 180 s, the light was removed).



Figure S17. Fitting curves of weight change over time of MOF-801, MIL-101 and M-8010 under 0.2 W/cm². Weight change (%) is relative to the mass of the adsorbed water.

Equaption	$\mathbf{y} = \mathbf{a} + \mathbf{b} \mathbf{x}$		
Sample	MOF-801	MIL-101	M-8010
a	-2.28103 ± 0.36888	-23.98438 ± 3.89328	-0.35332 ± 2.94789
b	-1.87449 ± 0.03894	-4.20424 ± 0.41096	-2.81302 ± 0.31117
Pearson's r	-0.99957	-0.99058	-0.98798
R-Square(COD)	0.99914	0.98125	0.97611
Adj. R-Square	0.99871	0.97187	0.96417

Table S5. The results about the fitting curves of weight change over time of MOF-801, MIL-101 and M-8010 under 0.2 W/cm^2 .



Figure S18. Fitting curve of weight change over time of MOF-801, MIL-101 and M-8010 under 0.4 W/cm². Weight change (%) is relative to the mass of the adsorbed water.

Table S6. The results about the fitting curves of weight change over time of MOF-801, MIL-101 and M-8010 under 0.4 W/cm².

Equaption	$\mathbf{y} = \mathbf{a} + \mathbf{b}^* \mathbf{x}$		
Sample	MOF-801	MIL-101	M-8010
a	0.2546 ± 0.34298	-4.04959 ± 4.48647	0.73746 ± 2.95906
b	-2.57426 ± 0.18333	-27.60331 ± 2.39812	-9.58702 ± 1.58168
Pearson's r	-0.99497	-0.99254	-0.97384
R-Square(COD)	0.98996	0.98513	0.94837
Adj. R-Square	0.98494	0.97769	0.92256



Figure S19. Fitting curve of weight change over time of MOF-801, MIL-101 and M-8010 under 0.6 W/cm². Weight change (%) is relative to the mass of the adsorbed water.

Table S7. The results about the fitting curves of weight change over time of	MOF-801,
MIL-101 and M-8010 under 0.6 W/cm ² .	

Equaption	$\mathbf{y} = \mathbf{a} + \mathbf{b} \mathbf{x}$		
Sample	MOF-801	MIL-101	M-8010
a	0.22315 ± 0.4142	-6.72414 ± 10.43709	1.1499 ± 1.6532
b	-5.63459 ± 0.2214	-34.31034 ± 5.57886	-10.34908 ± 0.88367
Pearson's r	-0.99846	-0.97457	-0.99279
R-Square(COD)	0.99692	0.94978	0.98563
Adj. R-Square	0.99538	0.92467	0.97844



Figure S20. A simple testing setup of light-driven water harvesting.



Figure S21. Optical pictures of the surface of the M-8010-based water harvester during the water release process.



Figure S22. The temperature and humidity change curves and optical pictures of the surface of the M-8010/CNTs water harvester during the water release process under light with 1 kW/m².