Supplementary Information

PPy-MOF-303@SA Aerogel Composite Adsorbent with Vertical Channels for Atmospheric Water Harvesting in Arid Environments: Preparation and Performance Evaluation

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Supplementary Section 1. Methods and Calculation

1.1 Preparation of MOF-303

Weigh 1.205 g of aluminum chloride hexahydrate and add 5.0 mL of deionized water. Stir to dissolve and set aside as Solution 1. Weigh 0.870 g of 3,5-pyrazoledicarboxylic acid monohydrate and 0.300 g of sodium hydroxide, then add 45.0 mL of deionized water. Stir to dissolve the ligands to obtain Solution 2. At a stirring speed of 100 rpm, pour Solution 1 into Solution 2 and continue stirring for 0.15 h. Then transfer the mixture into a 100.0 mL polytetrafluoroethylene autoclave and react at 120 °C for 24 h. Wash the product three times with deionized water and three times with anhydrous ethanol (8000 rpm, 10 min each). Finally, dry the product under vacuum at 60 °C to obtain MOF-303.

1.2 Preparation of PPy

Disperse 10.0 μL of pyrrole monomer in 10.0 mL of a mixed solvent of anhydrous ethanol and deionized water (volume ratio 1:1) using ultrasonication. Stir the mixture in an ice-water bath for 0.5 h. Subsequently, add 2.0 mL of an ammonium persulfate solution (0.16 $g\cdot mL^{-1}$) dropwise and continue stirring for reaction in the ice-water bath for 7 h. Collect the product by centrifugation and wash it with anhydrous ethanol until the supernatant becomes colorless and transparent. Finally, dry the product under vacuum at 60 °C for 24 h to obtain the product PPy.

1.3 Preparation of PPy@SA-d/MOF-303@SA-d

Add different masses of polypyrrole to a 1 wt% sodium alginate solution, with specific ratios referred to in (Table S1,Supporting Information). Pour the prepared gel precursor solution into a mold for directional freezing. Rapidly freeze the water in the precursor solution into ice using liquid nitrogen, and then freeze-dry it in a freeze dryer for 24 h. Subsequently, cross-link the material in a 2 wt% $CaCl_2$ solution for 12 h. Wash with deionized water to remove excess $CaCl_2$, followed by another 24 h of freeze-drying to obtain the product PPy@SA-d**(where "d" denotes directional freezing)**.MOF-303@SA-d was prepared using the same method, with specific ratios referred to in(Table S2,Supporting Information).

1.4 Preparation of PPy-MOF-303@SA-nd

Add different masses of polypyrrole and MOF-303 to a 1 wt% sodium alginate solution, with specific ratios referred to in (Table S4,Supporting Information). Pour the prepared gel precursor solution into a conventional mold. Rapidly freeze the water in the precursor solution into ice using liquid nitrogen, and then freeze-dry it in a freeze dryer for 24 h. Subsequently, cross-link the material in a 2 wt% $CaCl_2$ solution for 12 h. Wash with deionized water to remove excess $CaCl_2$, followed by another 24 h of freeze-drying to obtain the PPy-MOF-303@SA-nd ("nd" denotes non-directional freezing) aerogel with conventional pore channels.

1.5 Calculation of Desorption Activation Energy

The DTG curves of the material were measured using a thermogravimetric analyzer at heating rates of 4, 6, 8, 10, and 12 °C/min, with the temperature increasing from 30 °C to 140 °C. The desorption activation energy of the adsorbent was then calculated using the Kissinger equation, which is expressed as follows:

$$\ln\left(\frac{\beta}{RT^2}\right) = -\frac{E_d}{RT} - \ln\left(\frac{E_d}{k_0}\right) \quad (1)$$

In the equation, β represents the heating rate in °C/min; R represents the gas constant in J/(mol·K); T represents the peak desorption temperature in °C; and Ed represents the desorption activation energy in kJ/mol.

1.6 Evaluation of Adsorption Kinetics Using the LDF Model

The adsorption rate of the adsorbent was calculated with the Linear Driving Force (LDF) model. The original equation is:

$$\frac{d_{q_t}}{dt} = k(q_e - q_t) \quad (2)$$

Exponentiating both sides after integration：

$$q_t - q_e = A \cdot e^{-kt} \quad (3)$$

At the initial condition t=0,$q_t = 0$:

$$q_t = q_e(1 - e^{-kt}) \quad (4)$$

where q_t represents the dynamic adsorption capacity； q_e represents the equilibrium adsorption capacity； t represents time. k represents the adsorption rate constant，unit: min^{-1}； A is a constant.

Supplementary Section 2. Figures and Tables

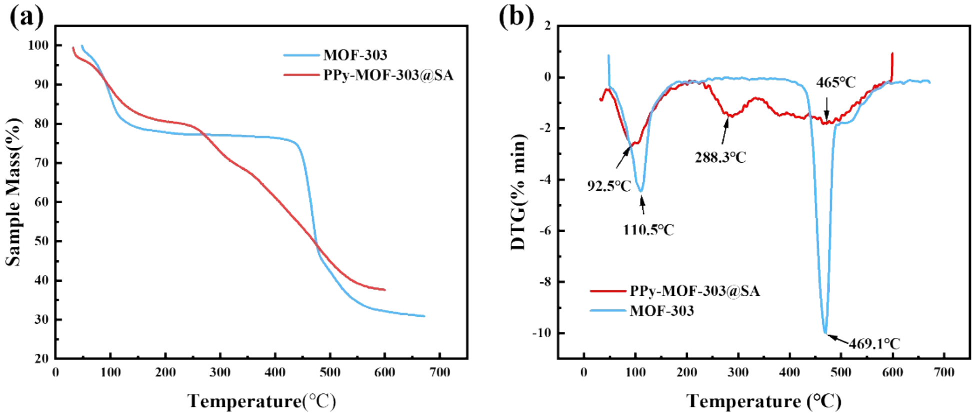

Fig. S1. (a) thermogravimetric curve and (b) DTG curve of the material under N2 atmosphere

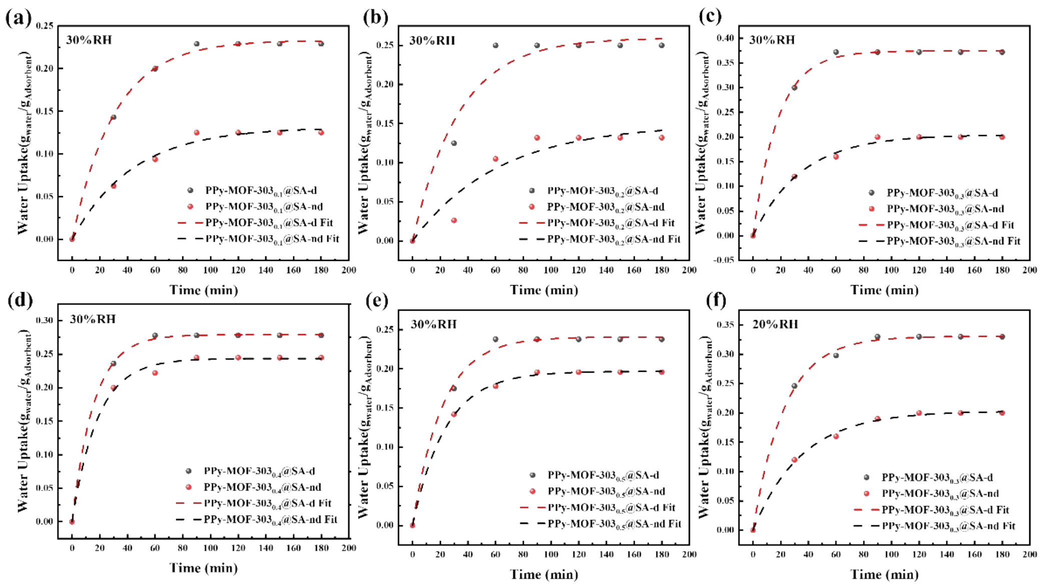

Fig. S2. (a-f) LDF model fitting of adsorption kinetics of composite adsorbents prepared by directed freezing and non-directed freezing

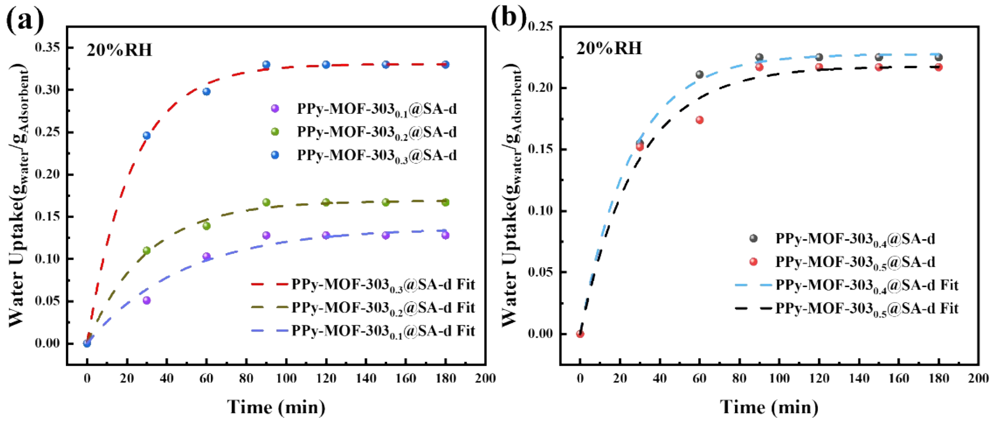

Fig. S3. (a,b) Adsorption kinetics and LDF model fitting results of composite adsorbents with different dosage of MOF-303 at 25 ℃ and 20% RH

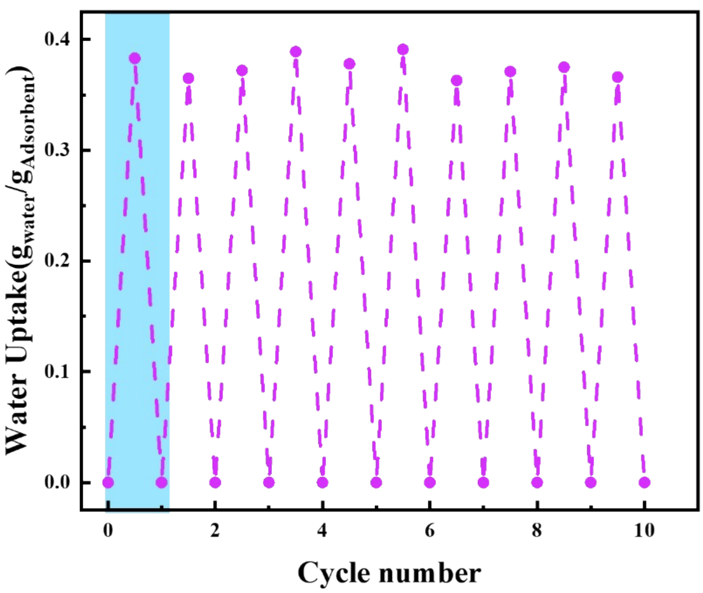

Fig. S4. Process of 10 vapor adsorption-desorption cycles at $PPy_{0.05}$-MOF-$303_{0.3}$@SA-d

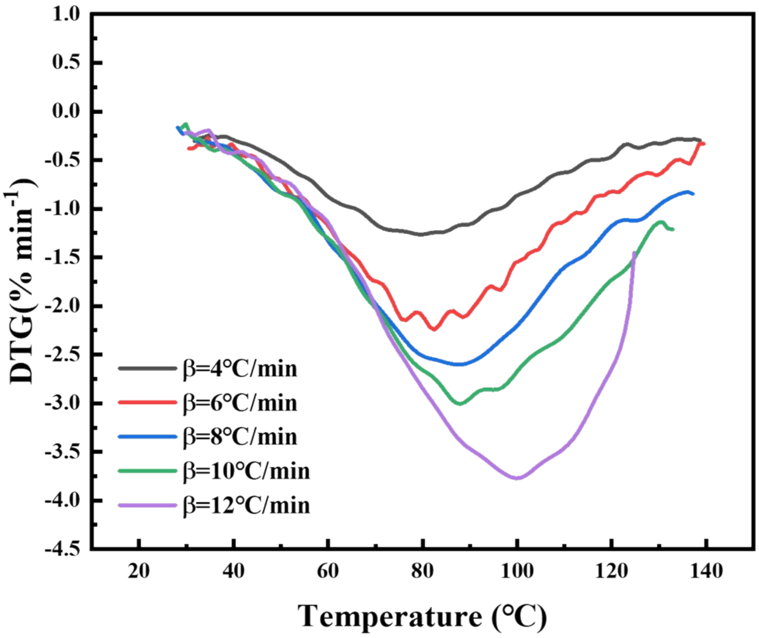

Fig. S5. DTG curves of the composite adsorbent at different heating rates in N_2 atmosphere

Table S1. detailed PPy additions in PPy@SA-d

Sample	$PPy_{0.02}$@SA-d	$PPy_{0.05}$@SA-d	$PPy_{0.075}$@SA-d	$PPy_{0.1}$@SA-d
PPy(g)	0.020	0.050	0.075	0.100

Table S2. MOF-303@SA-d lists the required MOF-303 additions

Sample	MOF-$303_{0.1}$@SA-d	MOF-$303_{0.2}$@SA-d	MOF-$303_{0.3}$@SA-d	MOF-$303_{0.4}$@SA-d	MOF-$303_{0.5}$@SA-d
MOF-303(g)	0.100	0.200	0.300	0.400	0.500

Table S3. PPy-MOF-303@SA-d lists the required MOF-303 additions

Sample	PP-MOF-$303_{0.1}$@SA-d	PPy-MOF-$303_{0.2}$@SA-d	PPy-MOF-$303_{0.3}$@SA-d	PPy-MOF-$303_{0.4}$@SA-d	PPy-MOF-$303_{0.5}$@SA-d
MOF-303(g)	0.100	0.200	0.300	0.400	0.500

Table S4. PPy-MOF-303@SA-nd lists the required MOF-303 additions

Sample	PP-MOF-$303_{0.1}$@SA-nd	PPy-MOF-$303_{0.2}$@SA-nd	PPy-MOF-$303_{0.3}$@SA-nd	PPy-MOF-$303_{0.4}$@SA-nd	PPy-MOF-$303_{0.5}$@SA-nd
MOF-303(g)	0.100	0.200	0.300	0.400	0.500

Table S5. pore structure parameters of PPy-MOF-303@SA obtained by mercury injection method

Porosity (%)	Bulk Density (g/cm^3)	Apparent Density (g/cm^3)	Average Pore Size A(nm)	Average Pore Size V(nm)	Total Pore Volume (cm^3/g)	Specific Surface Area (m^2/g)
92.1153	0.1011	1.2823	283.28	18082.83	9.1108	11.516

Table S6. LDF model fitting results of different MOF-303 additive amounts PPy-MOF-303@SA-d at 25 °C and 30% RH

Sample	PPy-MOF-$303_{0.1}$@SA-d	PPy-MOF-$303_{0.2}$@SA-d	PPy-MOF-$303_{0.3}$@SA-d	PPy-MOF-$303_{0.4}$@SA-d	PPy-MOF-$303_{0.5}$@SA-d
K(min^{-1})	0.03271	0.02989	0.05563	0.06336	0.04634
R^2	0.99789	0.96317	0.99872	0.99951	0.99581

Table S7. LDF model fitting results of different MOF-303 additive amounts PPy-MOF-303@SA-nd at 25 °C and 30% RH

Sample	PPy-MOF-$303_{0.1}$@SA-nd	PPy-MOF-$303_{0.2}$@SA-nd	PPy-MOF-$303_{0.3}$@SA-nd	PPy-MOF-$303_{0.4}$@SA-nd	PPy-MOF-$303_{0.5}$@SA-nd
K(min^{-1})	0.02298	0.0161	0.02883	0.05426	0.04198
R^2	0.98824	0.92013	0.99387	0.9962	0.99923

Table S8. LDF model fitting results of composite adsorbents with different MOF-303 additive amounts at 25 °C and 20% RH

Sample	PPy-MOF-$303_{0.1}$@SA-d	PPy-MOF-$303_{0.2}$@SA-d	PPy-MOF-$303_{0.3}$@SA-d	PPy-MOF-$303_{0.4}$@SA-d	PPy-MOF-$303_{0.5}$@SA-d	PPy-MOF-$303_{0.3}$@SA-nd
K(min^{-1})	0.02108	0.03354	0.04404	0.03972	0.03557	0.02849
R^2	0.97538	0.99535	0.99855	0.99867	0.98743	0.99773

Table S9. Peak desorption temperatures of PPy-MOF-303@SA at different heating rates

Adsorbent	T(℃)at different β(℃/min)					E_d(kJ/mol)
	4	6	8	10	12	
PPy/MOF-303	55.36	60.83	68.68	73.57	75.59	40.51