Electronic Supplementary Information

A Superhydrophobic and Porous Polymer Adsorbent with Large Surface Area

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1. Experimental Section

1.1 Synthesis of SHMP-1

0.3 mmol (0.14 g) 2-[3,5-di-(naphthalen-2-yl)-phenyl]-naphthalene (TNP, > 98 %, Extension Technology Co.) and 20 mL dichloromethane (DCM, > 99.9 %, Aladdin) were added into a 50 mL schlenk flask in N_2 atmosphere, stirring for 10 min until TNP was completely dissolved. Then, 14.4 mmol (1.92 g) anhydrous aluminum chloride ($AlCl_3$, > 99 %, Aladdin) was added, and heated to 40 °C for 24 h, followed by 80 °C for 24 h. The product was quenched with 100 mL dilute hydrochloric acid (V_{HCl}/V_{H2O}=2:1), washed three times with water and twice with ethanol. The product was finally dried in a vacuum oven for 24 h at 80 °C to get the brown powder of 0.172 g, i. e., the yield is 123 %, calculated from the mass of added monomers by the following equation S1.

$$Yield = \frac{M_1}{M_0} \times 100\ \% \quad \text{(S1)}$$

M_1 is the mass of the synthesized polymer (mg), M_0 is the mass of added monomers (mg).

1.2 Chemical stability tests of SHMP-1

30 mg of SHMP-1 was added in 30 mL HCl (5 mol/L) solution into a 40 mL bottle with the cap sealed. After 2 days, the HCl treated SHMP-1 was separated by filtration, washed with water three times and ethanol twice, then dried in vacuum oven at 80 °C for 24 h. The treatments of SHMP-1 by 5 mol/L NaOH solution and organic solvents (i.e., acetone, carbon tetrachloride, tetrahydrofuran and n-hexane) were the same with that of HCl solution.

1.3 Characterization of SHMP-1 and chemical treated SHMP-1

Contact angles of water and oil were measured by a contact angle meter (Dataphysics OCA20). 10 mg polymer was dispersed in 5 mL methanol, and then, dropped and coated on the double-sided adhesive (which has been pasted on a slide) in a spin coater at 1000 rmp/min for 10 min to get a macroscopically smooth surface for contact angle measurement. The volume of droplets of water or oil for contact angle measurement was 5 μL. Contact angle measurement was repeated 5 times to get an average value for polymer.

Adsorption-desorption isotherms of N_2 at 77 K and CO_2 at 273 K or 298 K on SHMP-1 were conducted on a AUTOSORB AS-1 physisorption analyzer (Quantachrome). SHMP-1 was outgassed overnight at 105 ^oC before N_2 and CO_2 adsorption experiment. Specific surface area of SHMP-1 was calculated from N_2 adsorption isotherm using the Brunauer-Emmett-Teller (BET) method in the relative pressure (P/P_0) range of 0.005−0.1. This range was obtained from Rouquerol plot of N_2 isotherm and is a linear region for the BET equation (Figure S9). Total pore volume and micropore volume were get from N_2 adsorption at P/P_0 =0.99 and P/P_0 =0.18, respectively. Pore size distribution (PSD) was calculated by the Nonlocal Density Functional Theory (NLDFT) method from the N_2 adsorption isotherm used the NLDFT equilibrium model of N_2 at 77 K on carbon with slit pores and Grand Canonical Monte Carlo (GCMC) method from the CO_2 adsorption isotherm measured at 273 K. Fourier transform infrared (FTIR) spectra of SHMP-1 and TNP were recorded in the range from 4000 to 500 cm^{-1} (Bruker-vector-22). SHMP-1 and TNP were mixed with KBr, ground in agate mortar, and then pressed to a tablet for FTIR measurement. Solid-state ^{13}C cross-polarization

magic-angle spinning nuclear magnetic resonance (^{13}C CP/MAS NMR) spectrum of SHMP-1 was recorded on a 400 MHz Bruker Avance Ⅲ HD at a spinning frequency of 9 kHz (contact time of 3 ms and pulse delay for 5 s) using a 4 mm double channel MAS probe. Thermogravimetric analysis (TGA) of SHMP-1 was carried out on a PerkinElmer Instrument Pyris1 TGA in the range of 50-850 ^{o}C at the heating rate of 10 ^{o}C /min in oxygen atmosphere. Field emission scanning electron microscopy (FE-SEM) images and energy dispersive spectroscope (EDS) mapping of SHMP-1 were collected by a Zeiss GEMINI 300 with the scanning voltage of 1 kV. For SEM observation, 2 mg polymer powders were dispersed in 10 mL n-hexane by 30 min ultra-sonication, and then, dropped on a silicon wafer to form a film after evaporation of n-hexane. Powder X-ray diffraction (XRD) pattern of SHMP-1 was recorded on an D/max-2550 X-ray diffractometer (Rigaku) from 3° to 77° with a scan step size of 0.02° at 40 kV using Cu/Kα radiation. 100 mg of polymer powder was used to test particle sizes by the bluewave s3500 laser particle size meter (Microtrac).

1.4 Adsorption-desorption experiment of water vapor

Adsorption-desorption of water vapor on SHMP-1 was determined at the relative humidity in the range of 0% to 90% at 25 ^{o}C by the AQUADYNE DVS water vapor adsorption instrument (Quantachrome) with a quartz balance. Adsorption equilibrium was assumed to be reached when the weight change of sample was less than 0.1 μg within 10 min at a given relative humidity. Before adsorption, SHMP-1 was outgassed in vacuum at 105 ^{o}C overnight.

1.5 Absorption experiment of organic solvents

Organic solvents absorption were carried out at 25 °C in both of the syringes and the vials according to the procedures reported by Kim et al. (*Chem. Mater*, **2019**, 31, 5206) and Li et al. (*Energy Environ. Sci*, **2011**, 4, 2062), respectively. After outgassed in a vacuum at 105 °C overnight, 100 mg SHMP-1 was filled into a 10 mL syringe with tip blocked by 10 mg fiberglass. Then, organic solvents were dropped into the tip blocked syringes with or without filled SHMP-1 until the solvent flowed out from the tip. After 2 min without solvent flowed out from the tips, both of the syringes with or without filled SHMP-1 were weighted to get the absorbed mass of organic solvents. For vial experiment, 100 mg outgassed SHMP-1 and 3mL organic solvents were mixed in 8 mL vials for 5 min. Then, SHMP-1 were separated by centrifugation at 3500 r/min for 15 min, and weighted to get the absorbed mass.

1.6 Breakthrough experiments of CO_2 with or without water vapor

Breakthrough experiments of CO_2 with or without water vapor were conducted at 298 K and 1 bar by setting up an instrument following the schematic diagram shown in Figure S10. SHMP-1 (1.1356 g) was placed in the column fixed bed (10 mm in diameter and 7 cm in length), activated at 378 K under vacuum for 24 h, and purged using He gas for 1h at 1.0 bar before breakthrough experiment. Then, adsorption of CO_2 was performed with or without water vapor at a total feed flow rate of 10 mL/min. Water vapor was introduced by the CO_2 gas passing through a temperature-controlled humidifier. Relative humidity (RH) was controlled by mixing the gas flow of CO_2 passed from temperature-controlled humidifier and another gas flow of dry CO_2. The adsorption capacity of CO_2 was calculated using the following equation S2 from the breakthrough curves.

$$Q_{adsorption} = V_{input} C_{n0} \Delta t - \int_0^t V_{influent} C_{nt} dt \qquad (S2)$$

Where $Q_{adsorption}$ is the adsorption capacity of CO_2 (cm^3) at time t, V_{input} and $V_{influent}$ is the input and effluent flow rate (cm^3/min) respectively, C_{n0} and C_{nt} is the input and effluent CO_2 concentration (mg/m^3) respectively, and Δt is the breakthrough time (min).

1.7 Structure simulation of SHMP-1

Structure of SHMP-1 was simulated by Accelrys' Material Studio (MS) v.8.0 software. The particular model was constructed from a combination of clusters containing 147 carbon atoms. Each cluster was relaxed fully using the Discover module and the COMPASS force-field twice to ensure the cell parameters as well as the density remained constant. Then, a Connolly surface was established to model the structure using Atom, Volumes and Surface tool and employing a fine grid resolution (0.25 Å) and a Connolly kinetic radius for N_2 of 1.82 Å. The interconnected micropore structure was simulated by packing amorphous cells with periodic boundary conditions. Pore widths were estimated from two-dimensional slices of the simulated pore structure. This model simulates the microporosity only but not the mesoporosity and the macroporosity.

Table S1. Summary of superhydrophobic materials with their water contact angles (WCA), specific surface area (S_{BET}) and pore volume values.

Samples	WCA(°)	S_{BET} (m^2/g)	Pore volume (cm^3/g)	References
SHMP-1	167	2100	1.20	This work
OPA-PCN-222	157	1617	-	*J. Mater. Chem. A* **2017**, *3*, 16213
OPA-UiO-66-SO_3H	162	1148	-	*J. Mater. Chem. A* **2017**, *3*, 16213
COF-DTF	>150°	1056	1.75	*ACS Appl. Mater. Inter.* **2019**, *12*, 2926
COF-VF	167°	938	-	*Chem* **2018**, *4*, 1726
PANI	165	835.7	-	*J. Mater. Chem. A* **2015**, *3*, 19299
ZCMP-1	153.9	691	0.416	*J. Mater. Chem. A* **2018**, *6*, 8633
PG	160	653	0.226	*Adv. Mater.* **2017**, *29*, 1605307
Sponge@HFGO@ZIF-8	162	590	-	*Angew. Chem. Int. Edit.* **2016,** *55*, , 1178
IISERP-COF_2	161	584	-	*J. Mater. Chem. A* **2017**, *5*, 8376
PTSA to cotton	157	477	0.60	*J. Mater. Chem. A* **2015**, *3* , 16213
PVA-3	156.6	425.3	-	*Adv. Funct. Mater.* **2017**, *27*, 1604423
CNP	163	366	-	*J. Am. Chem. Soc.* **2018**, *140*, 13786
HMDS/ZSAs	154	174.4	0.725	*J. Mater. Chem. A* **2016**, *4*, 5632
RGO/PC	161	137.2	-	*Carbon* **2011**, *49*, 5166
PVDF/graphene	153	131.3	-	*J. Mater. Chem. A* **2014**, *2*, 3057
GA	153.9	117	0.991	*J. Mater. Chem. A* **2015**, *3*, 7498

115 **Table S2. Absorption capacity of organic solvents by superhydrophobic materials.**

Materials	S_{BET} (m^2/g)	Organic solvents	Absorption capacity (g/g)[a]	Absorption capacity (mmol/g)[b]	Absorption capacity (mL/g)[b]	References
SHMP-1	2100	1,2-dichlorbenzene	25.00	170	19.48	This study
		Nitrobenzene	18.20	148	15.04	
		Benzene	11.80	151	13.41	
		DMSO	10.22	128	9.18	
		DMF	8.91	122	9.48	
		Methanol	4.09	128	5.19	
OPA-UiO-66	1068	Toluene	3.50	*38*	*4.02*	*J. Mater. Chem. A* **2017**, *5*,18770
		DMF	3.52	*48*	*3.74*	
		Chloroform	2.02	*17*	*1.36*	
		Acetone	1.48	*26*	*1.87*	
		Methanol	1.60	*34*	*2.02*	
HCMP-2	928	1,2-dichlorbenzene	24.03	*163*	*18.46*	*Energy Environ. Sci.* **2011**, *4* , 2062
		Benzene	10.64	*83*	*7.39*	
		DMSO	6.08	*78*	*12.27*	
		Nitrobenzene	16.20	*130*	*13.22*	
		Methanol	4.74	*148*	*8.86*	
		Ethanol	6.02	*131*	*7.59*	
		Acetone	6.03	*104*	*7.65*	
		THF	11.3	*152*	*12.54*	
		Ethylbenzene	11.5	*108*	*13.21*	
		Chloroform	13.5	*113*	*9.12*	
		Phenol	9.9	*107*	*9.34*	
		Hexane	5.8	*67*	*8.78*	
COP-177	536	DMF	8.89	115	8.88	*Chem. Mater.* **2019,** *31*, 5206
		THF	6.10	88	7.10	
		Methanol	2.94	136	5.52	
		Toluene	6.41	66.6	7.08	
		Chloroform	11.23	94	7.54	
HFGO@ ZIF-8	590	DMSO	7.49	*96*	*6.81*	*Angew. Chem. Int. Edit.* **2016,** *55*, 1178
		DMF	0.950	*13*	*13.83*	
		Veg oil	2.01	/	/	
		Coconut oil	2.23	/	/	
		Petroleum ether	1.90	/	/	
PP/mnPTFE	/	DMSO	7.49	*96*	*6.81*	*ACS Appl. Mater. Inter.* **2019,** *11*, 7479
		Benzene	6.94	*89*	*7.89*	
		Chloroform	8.30	*70*	*5.61*	
		Dichloroethane	9.10	*96*	*7.37*	
		Olive oil	5.98	/	/	

116 [a] reported in the literatures, [b] reported data or calculated data (italic) from the mass adsorption capacity with molecular weight
117 or density. /: not available.

Table S3. The weight recovered and percent recovery of SHMP-1 (30 mg) after 2 day immersion in 5M HCl and 5M NaOH solution or organic solvents.

solvents	recovered weight (mg)	recovery rate (%)
HCl	29.7	99.0
NaOH	29.6	98.7
Ethanol	29.6	98.7
Acetone	29.5	98.3
Carbon tetrachloride	29.5	98.3
Tetrahydrofuran	29.6	98.7
n-Hexane	29.7	99.0

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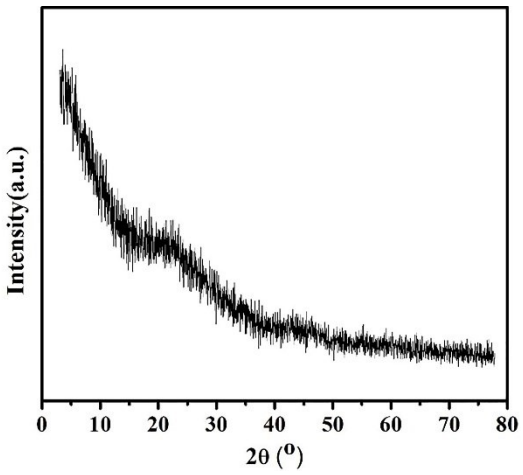

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123 Figure S1. Powder XRD pattern of SHMP-1.

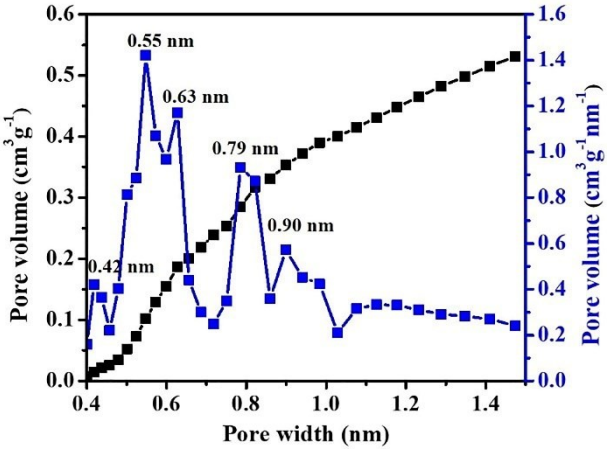

Figure S2. GCMC-PSD from CO_2 adsorption isotherm at 273 K.

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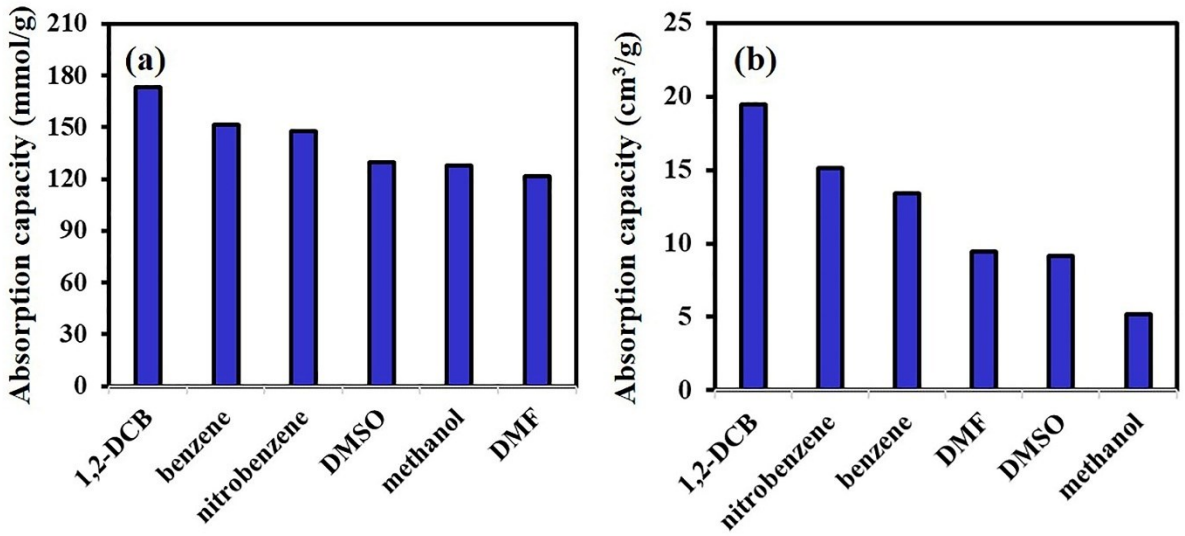

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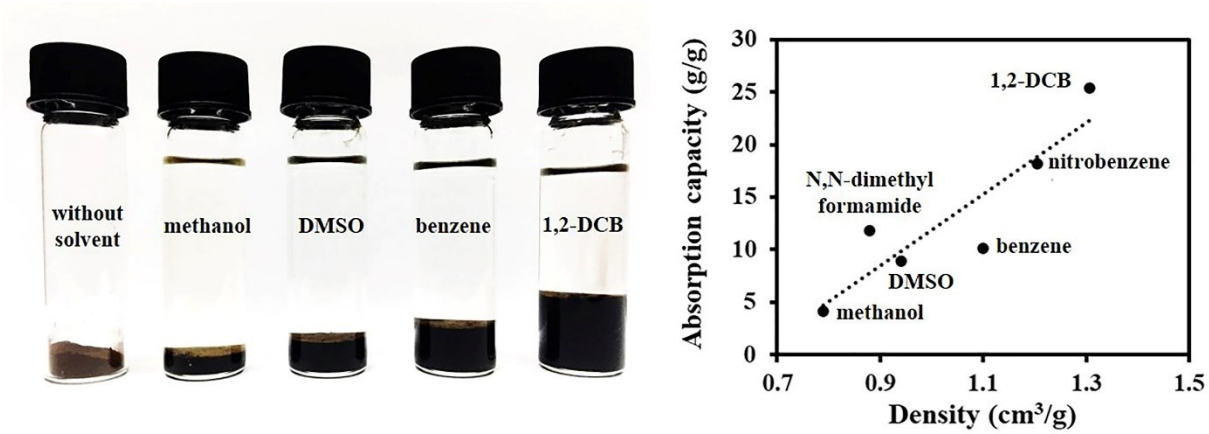
128 Figure S3. Absorption capacity of organic solvents by SHMP-1 in molar unit (mmol/g) and

129 volumetric unit (cm^3/g).



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131 Figure S4. Photograph of 150 mg SHMP-1 without solvent or with 7 mL 1,2-dichlorobenzene
132 (1,2-DCB), benzene, dimethyl sulfoxide (DMSO) and methanol as well as the linear
133 relationship of uptake capacity of organic solvents by SHMP-1 with their density.

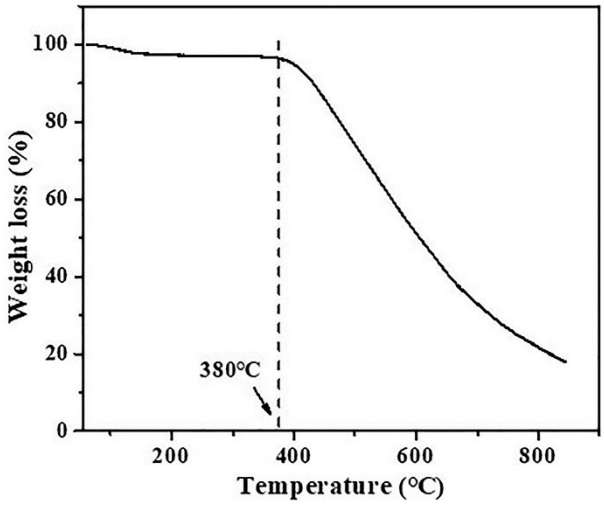

Figure S5. Thermogravimetric (TG) curve of SHMP-1.

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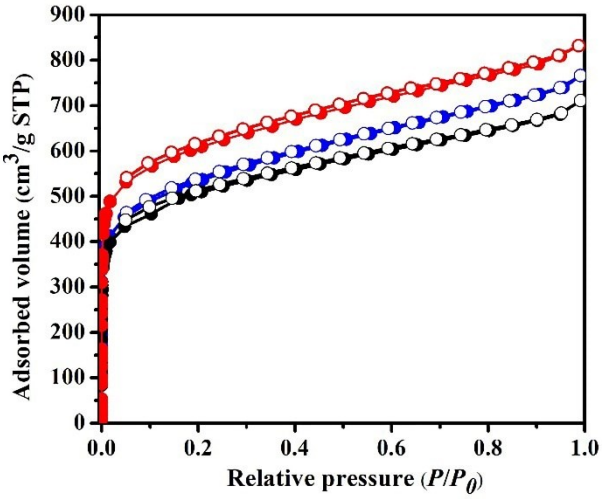

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139 Figure S6. Nitrogen adsorption-desorption isotherm (77K) of SHMP-1 (red), 5 mol/L

140 HCl immersed SHMP-1 (blue) or 5 mol/L NaOH immersed SHMP-1 (black).

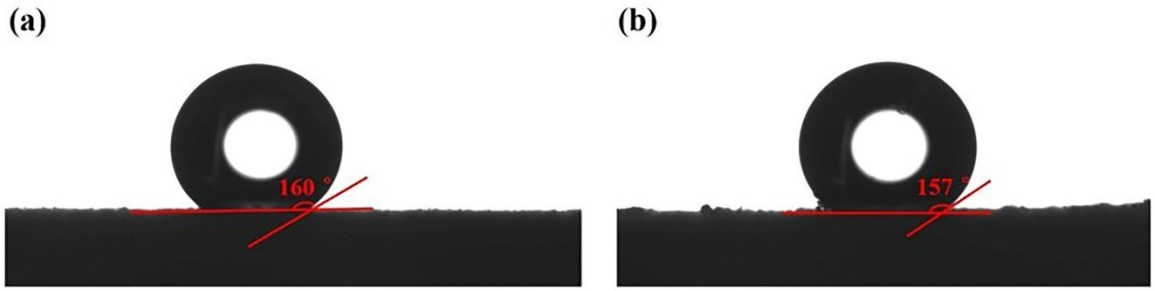
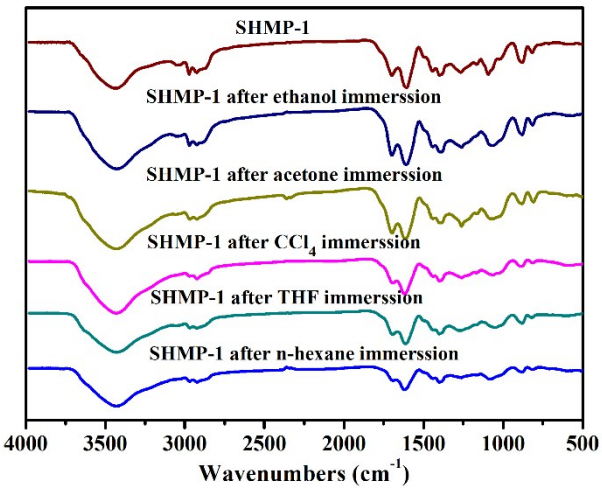


Figure S7. Water contact angle of SHMP-1 after immersed in 5 mol/L HCl (a) and 5 mol/L NaOH (b) for 2 days.



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145 Figure S8. FTIR spectra of SHMP-1 after immersed in ethanol, acetone, carbon

146 tetrachloride (CCl4), tetrahydrofuran (THF) and n-hexane for 2 days.

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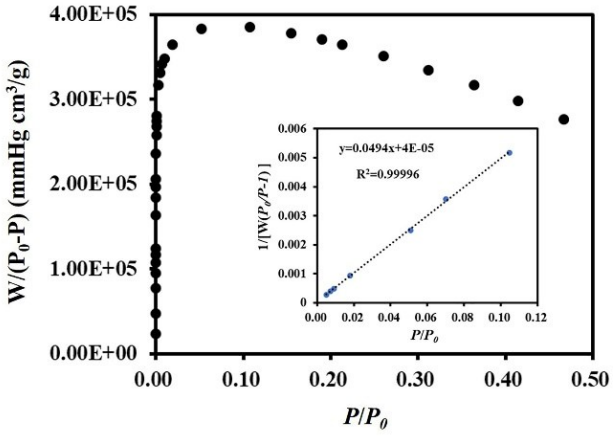

Figure S9. Rouquerol plot, i.e., $W/(P_0-P)$ *vs*. P/P_0, of SHMP-1 from N_2 isotherm. Only the range below $P/P_0 = 0.10$ satisfies the first consistency criterion for applying the BET theory. The inset plot is the linear region for the BET equation.

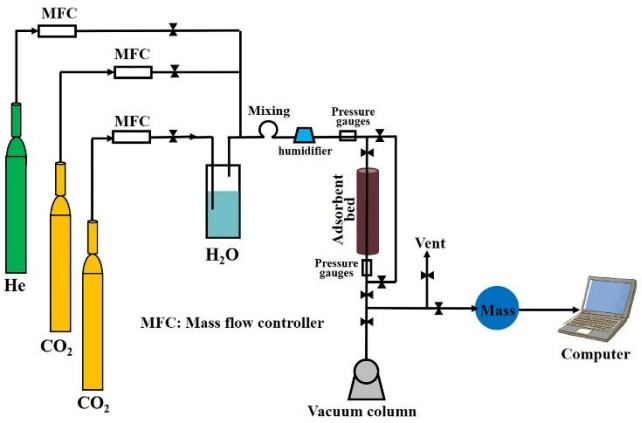

Figure S10. Schematic diagram of breakthrough experiment for CO_2/H_2O adsorption.