Electronic Supplementary Material (ESI) for Green Chemistry.
This journal is © The Royal Society of Chemistry 2015

Supplementary Information for

Facile synthesis of amine hybrid aerogel with high adsorption efficiency and regenerability for air capture via solvothermal-assisted sol-gel process and supercritical drying

Yong Kong,[a,b] Xiaodong Shen,*[a,b] Sheng Cui[a,b] and Maohong Fan*[c,d]

[a] College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, China

[b] State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing 210009, China

[c] Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie, WY 82071, USA

[d] School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

* To whom correspondence should be addressed. E-mail: xdshen@njtech.edu (Xiaodong Shen); mfan@uwyo.edu (Maohong Fan)

Supercritical drying (SCD) procedure

SCD was performed using Helix 2 Liter System (Applied Separations, Inc., Allentown, PA). The photo and flow diagram of the SCD apparatus is present in Fig. S1. Wet gel was put into the separator vessel (SV). The pressure of the SV was raised up to 10±0.2 MPa by a CO_2 pump. Ethanol in the wet gel was first replaced by liquid CO_2 at room temperature (25±2 °C) until there was no ethanol out from the CV bottom outlet, the flow rate of liquid CO_2 was regulated at 15±2 SLPM by the back pressure regulator. Then the temperature of the SV was raised to 50 °C and maintained at the same temperature for 4 h to make sure that the ethanol was completely displaced by supercritical CO_2, the CO_2 flow rate during this period was maintained at 9±1 SLPM. During these operations, the pressure of the SV was maintained at 10 MPa±0.2 by the CO_2 pump. At the end, the SV was depressurized to atmospheric pressure with a flow rate being 5±1 SLPM to obtain AH-RFSA (Fig. S2).

Calculation of the CO_2 adsorption and desorption capacity

The CO_2 adsorption profile of the blank and AH-RFSA-50 with dry air at 25 °C is presented in Fig. S3. The regions which represent the total CO_2 adsorption capacity and useful CO_2 adsorption capacity are marked in Fig. S3. As presented in Fig. S4, the total CO_2 adsorption capacity can be calculated by subtracting A2 (gray region) from A1 (gray region). The calculation methods for the CO_2 capacity of A1 and A2 are same. Fig. S5 depicts the schematic diagram for calculating the CO_2 capacity of A2. The time (t) can be divided into numbers of Δt *(s).* During Δt, the CO_2 capacity is described as eq. S1

$$\Delta A_{i,CO_2}(mmol) = \frac{C_i + C_{i+1}}{2 \times 100} \times \Delta V_i \div 22.4 \times 1000 \qquad \text{(S1)}$$

Where C_i (%) is the CO_2 concentration recorded by gas analyzer at t_i, ΔV (L) is the gas volume flowed through the fixed bed during Δt.

$$\Delta t = t_{i+1} - t_i \quad i=0, 1, 2, 3... \qquad \text{(S2)}$$

In this research, the data is recorded once per second, i. e. $\Delta t = 1$.

The flow rate v (ml/min) during the test is constant and calibrated to 300 ml/min at standard state, ΔV can be written as

$$\Delta V_i = \frac{\Delta t \times v}{1000 \times 60} \qquad \text{(S3)}$$

The CO_2 capacity of any Δt can be written as

$$\Delta A_{i,CO_2}(mmol) = \frac{(C_i + C_{i+1}) \times \Delta t \times v}{2 \times 100 \times 60 \times 22.4} = \frac{C_i + C_{i+1}}{896} \tag{S4}$$

The CO_2 capacity of A1 can be described as eq. S5, where m (g) is the weight of the sorbent.

$$Capacity(mmol/g) = \frac{\sum_{0}^{i} \Delta A_{i,CO_2}}{m} \tag{S5}$$

Similarly, the CO_2 capacity of A1 is obtained. Thus, the total CO_2 adsorption capacity of the adsorbent can be obtained. The useful CO_2 adsorption capacity and CO_2 desorption capacity are also obtained by using the calculation method of A2.

CO_2 adsorption capacity and surface amine content of AH-RFSA with different R:APTES ratios

The CO_2 adsorption capacities and surface amine (N) contents from XPS test of the adsorbents with different R:APTES ratios are summarized in Table S3. It suggests that higher APTES (amine) ratio in the reactants should lead to higher CO_2 adsorption capacity and surface amine content.

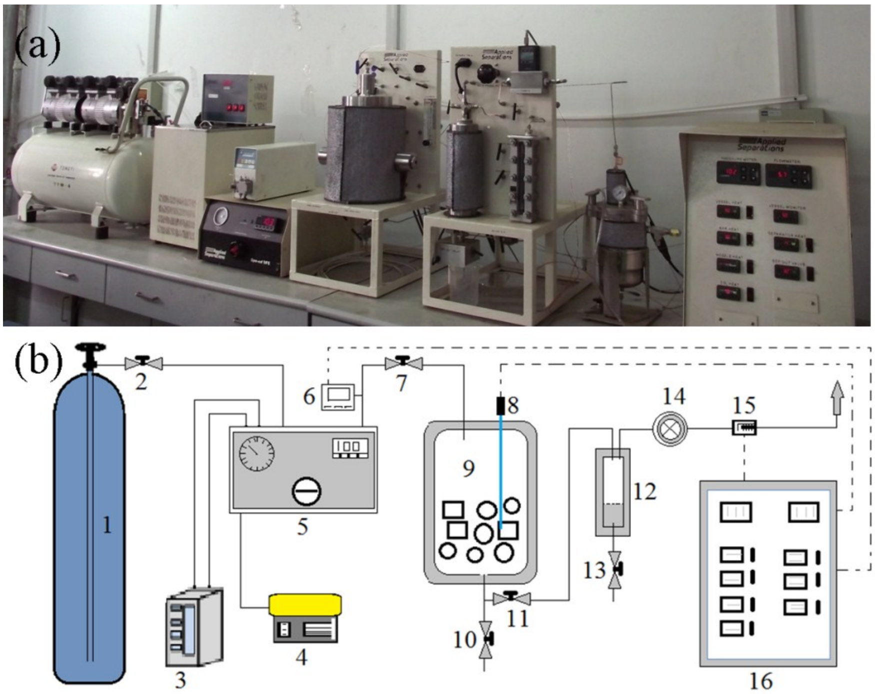

Fig. S1 (a) Photo of the SCD apparatus and the corresponding (b) SCD flow diagram: (1) liquid CO_2 cylinder; (2) liquid CO_2 valve; (3) cooling circulating bath; (4) air compressor; (5) CO_2 pump; (6) pressure senor; (7) CO_2 inlet valve; (8) thermal couple (9) separator vessel (SV); (10) SV bottom vent valve; (11) SV bottom outlet valve; (12) collector vessel (CV); CV bottom outlet valve; (14) back pressure regulator; (15) mass flow meter with temperature and pressure sensors; (16) main controller.

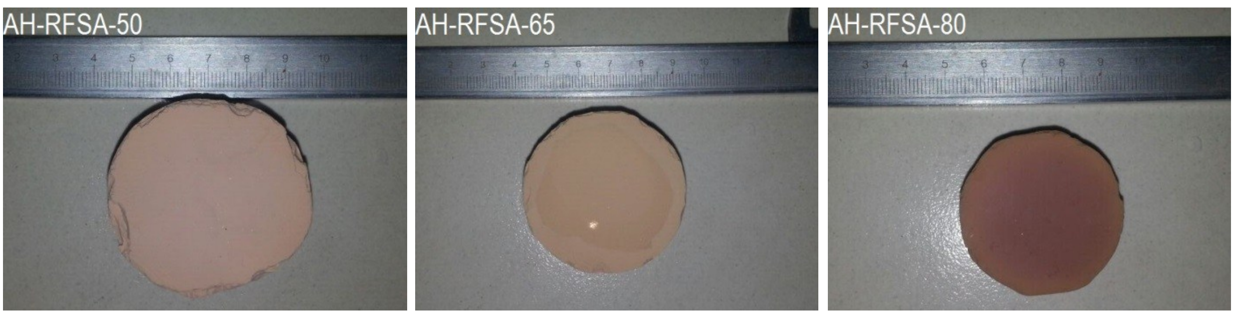

Fig. S2 Photographs of AH-RFSA-50, AH-RFSA-65 and AH-RFSA-80.

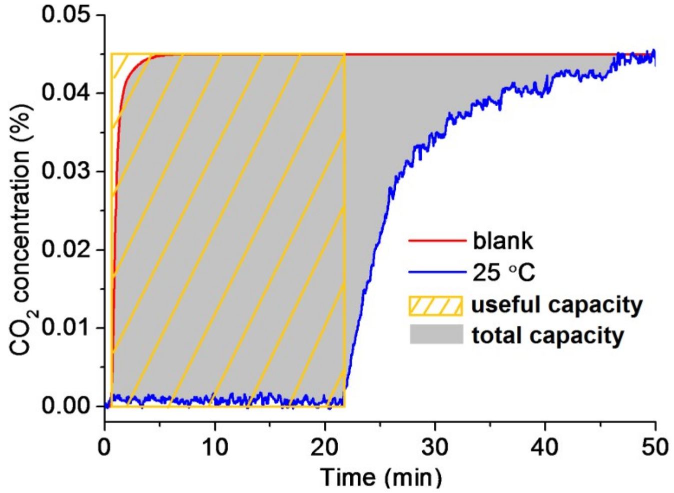

Fig. S3 CO_2 sorption profiles of blank and AH-RFSA-50, and the instructions of the total and useful CO_2 adsorption capacity.

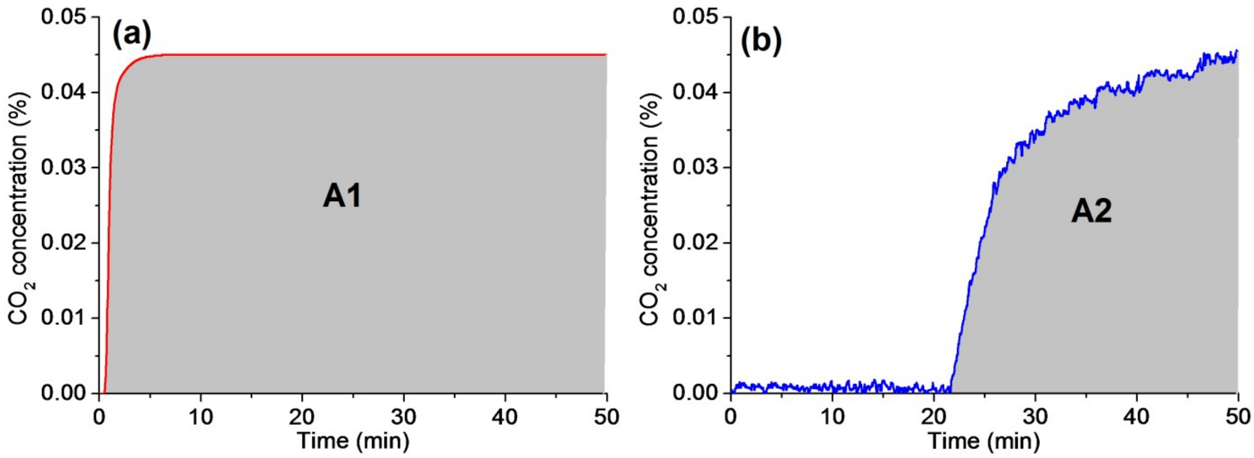

Fig. S4 Introductions for the calculation of CO_2 capacity: (a) CO_2 adsorption profile of blank; (b) CO_2 adsorption profile of AH-RFSA-50.

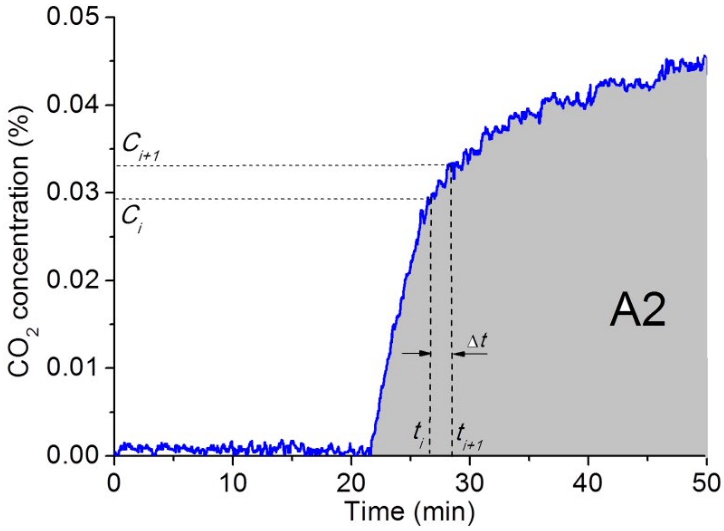

Fig. S5 Schematic diagram for calculating CO_2 capacity of region A2.

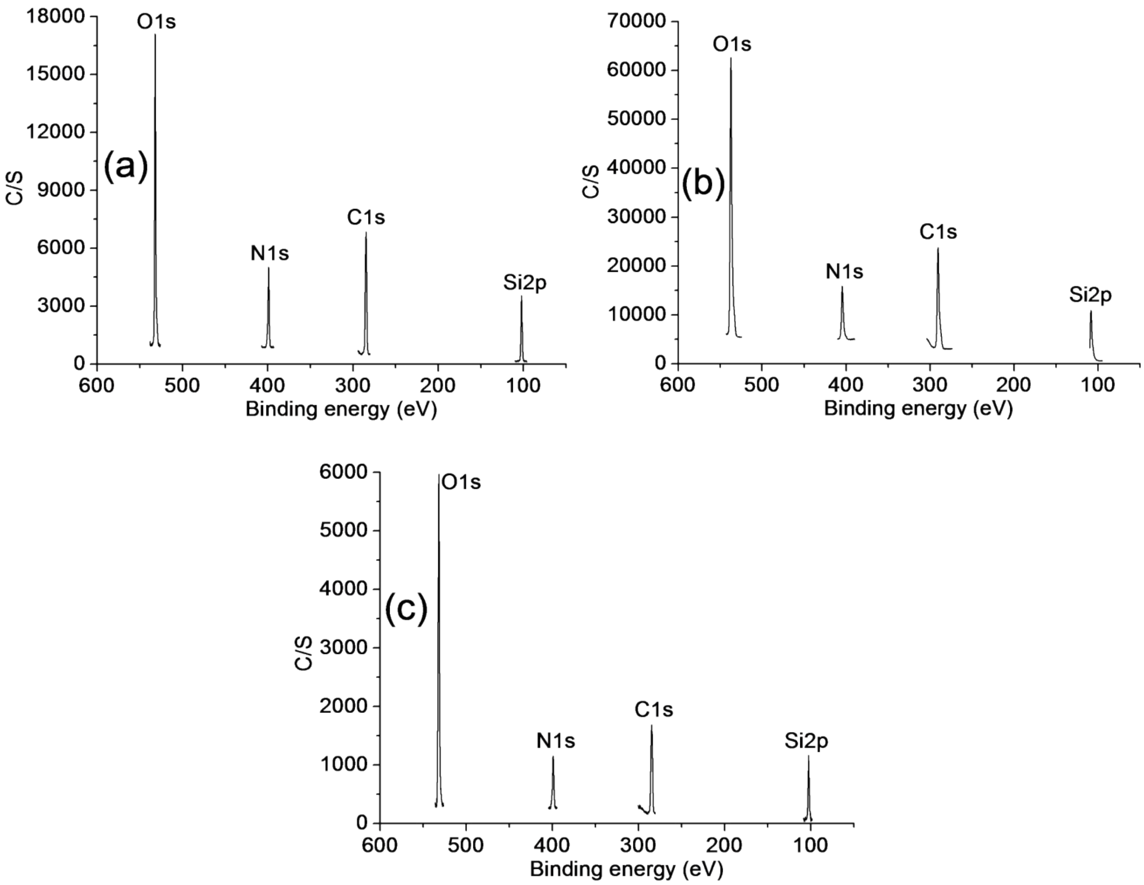

Fig. S6 XPS data of (a) AH-RFSA-50, (b) AH-RFSA-65 and (c) AH-RFSA-80.

Table S1 Amine contents, percentages of inorganic and organic moiety of AH-RFSA

Sample	Inorganic moiety content (%)	Organic moiety content (%)	Amine content (mmol/g)
AH-RFSA-50	37.9	62.1	7.68
AH-RFSA-65	28.0	72.0	6.48
AH-RFSA-80	16.5	83.5	5.99

Table S2 Surface amine (N) contents and CO_2 adsorption capacities of AH-RFSA with different R:APTES ratios (solvothermal temperature of 50 °C; adsorption with dry air).

R:APTES	Surface amine content (mmol/g)	CO_2 adsorption capacity (mmol/g)
1:8	7.02	1.59
1:9	7.45	1.71
1:10	7.68	1.80