Supporting Information

Support-Free Porous Polyamine Particles for CO_2 Capture

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General Methods. *N*-Vinylformamide (Sigma-Aldrich) was vacuum-distilled. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Other chemicals were used as received from commercial sources. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance-300 spectrometer. Chloroform-*d* (D, 99.8%) was purchased from Cambridge Isotope Laboratories, Inc. High resolution mass spetra were obtained using Qstar XL QqTOF instrument with an ESI source. FTIR was performed using a Varian 640-IR spectrometer and KBr was used as the background. A Philips XL-30 ESEM FEG instrument was operated at 2 kV to obtain the SEM images after the samples were coated by Au.

Comparison of FTIR Spectra of Polyamine Particles Prepared Using Different Protocols. As described in the main text, the polyamine particles were prepared by precipitation polymerization using two different protocols. One protocol involved heating the monomer/crosslinker mixture initially at 60 ^{o}C for 12 h and then at 70, 80, and 90 ^{o}C each for 1 h. The other protocol was invoked in a control experiment. It involved polymerizing the mixture at 90 ^{o}C for 4 h. Figure S1 compare the FTIR spectra of particles generated from the different protocols. The peaks at 887 and 762 cm^{-1} were due

to the alkene *trans* and *cis* C-H out of plane bends. These peaks were weak for the sample prepared using the staged heating protocol but strong for the sample prepared by heating at 90 ^{o}C for 4 h. Therefore, the double bond conversion of the particles prepared using the staged heating or standard protocol was higher.

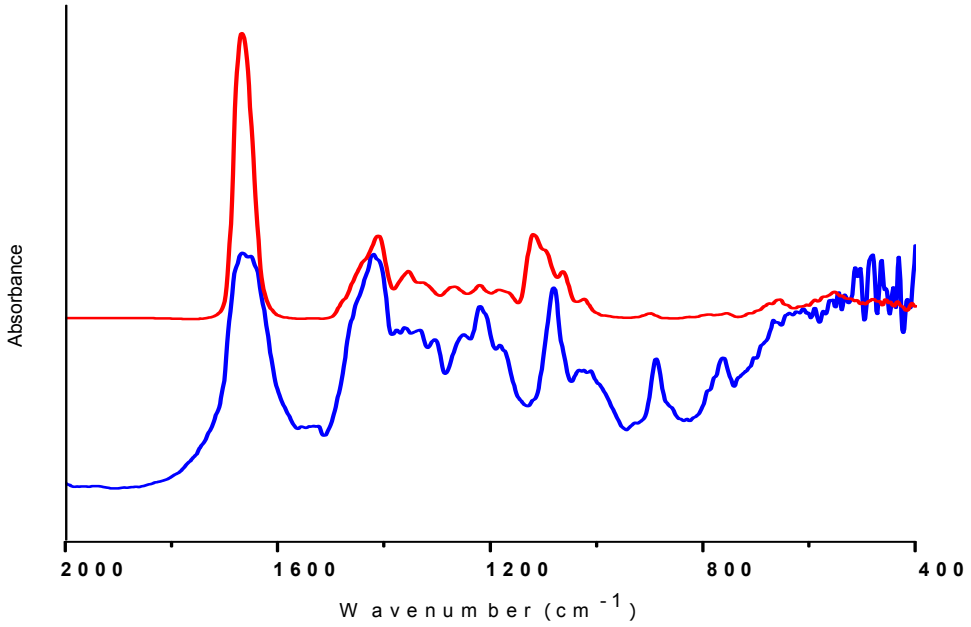

Figure S1. FTIR spectra for the precipitation polymerization products prepared at 90 ^{o}C for 4h (blue) and via staged heating (red).

AFM of the Polyamine Particles Prepared Using the Standard Protocol. Specimens were prepared for atomic force microscopy (AFM) analysis via aero-spraying the sample solutions onto freshly cleaved mica surfaces. Because the solution was atomized, the water spray evaporated within seconds. AFM analysis was performed in the trapping mode using a Veeco multimode instrument equipped with a Nanoscope IIIa controller.

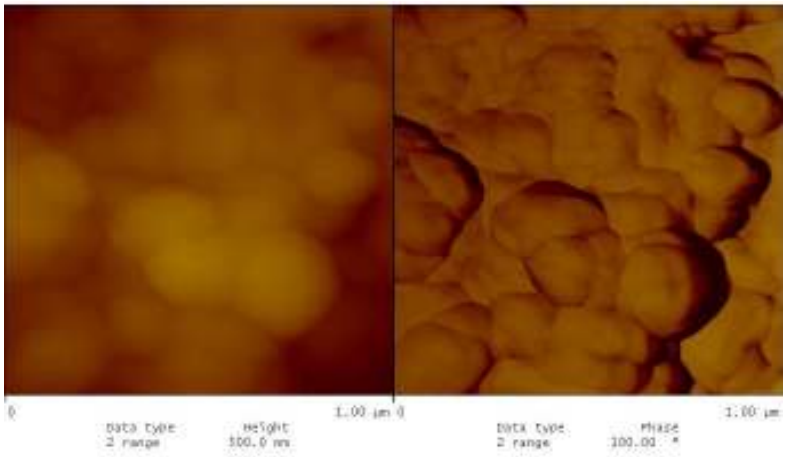

Figure S2. AFM topography (left) and phase (right) images of the polyamine particles.

TGA of the Polyamine Sample. Thermogravimetic analysis (TGA) of the polyamine particles was performed using a TA Q-500 analyzer and the sample was heated at a rate of 10 ^{o}C/min from room temperature to 600 ^{o}C in a nitrogen atmosphere.

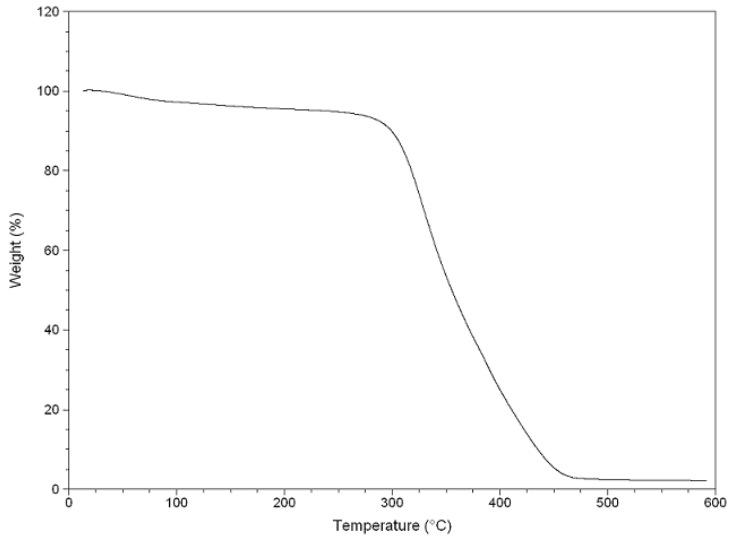

Figure S3. TGA curve for the polyamine particles.

***N*-Methyl-*N*-vinylformamide.** *N*-Vinylformamide (1.42 g, 20 mmol) was mechanically stirred in anhydrous THF (80 mL) at 0 ^{o}C under a N_2 atmosphere and potassium *tert*-

butoxide (2.15 g, 21 mmol) was added in three portions. The mixture was vigorously stirred for 30 min and iodomethane (2.85 g, 20 mmol) was then added dropwise. The reaction solution was stirred for 24 h at room temperature. This solution was subsequently filtered and THF was removed under reduced pressure. The crude product was purified via silica chromatography (ethyl acetate / hexane = 1:3, v/v) to give a colorless liquid (0.75 g, 44% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.31, 8.11 (2s, H, -C(=O)H), 7.35, 6.69 (dq, J = 8 Hz, 1H, CH_2=CH-), 4.52 (dd, J = 8 Hz, 2H, CH_2=CH-), 3.02 (s, 3H, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 162.5 (-HC=O), 134.3 (CH_2=CH-), 93.6 (CH_2=CH-), 26.6 (-CH_3); EI-HRMS (ESI, *m/z*): calcd for C_4H_7NO, 85.0528; found, 85.0526.

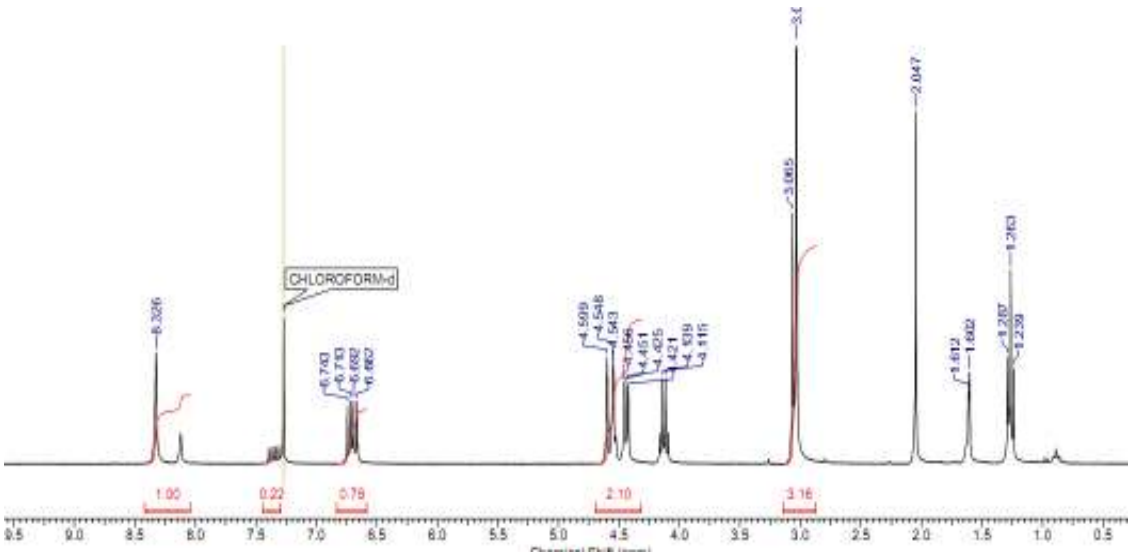

Figure S4. ^{1}H NMR spectrum of *N*-methyl-*N*-vinylformamide in $CDCl_3$.

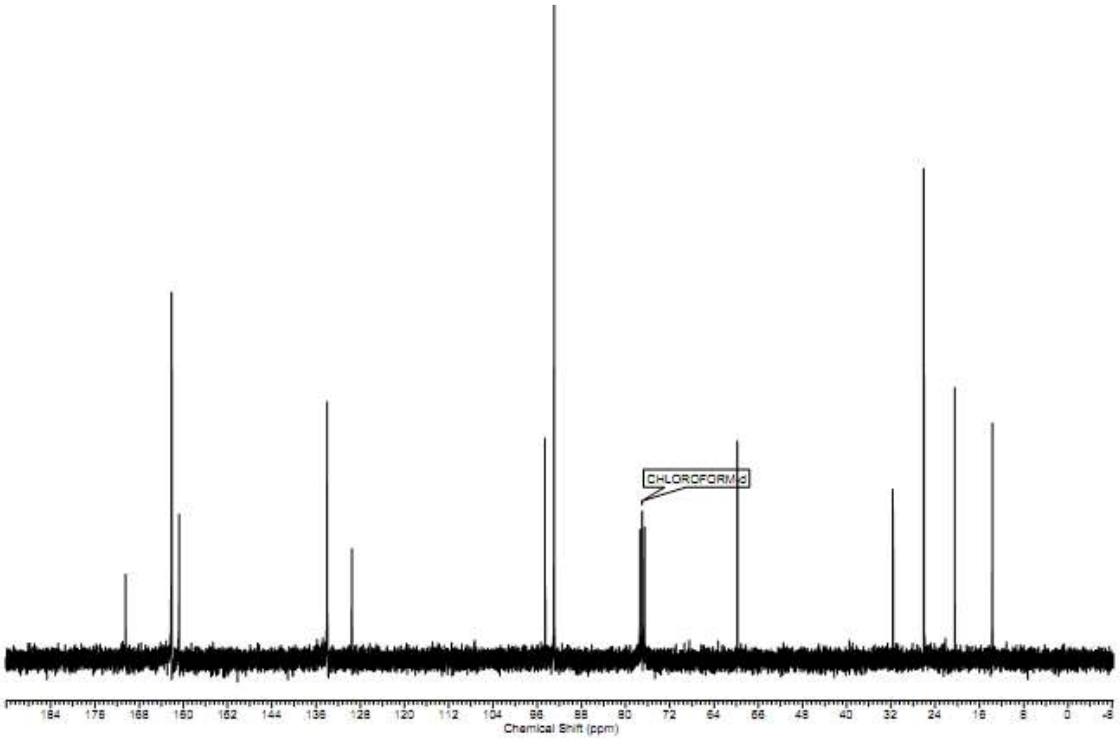

Figure S5. ^{13}C NMR spectrum of *N*-methyl-*N*-vinylformamide in $CDCl_3$.

Di[2-(*N*-vinylformamido)ethyl] ether. *N*-Vinylformamide (6.39 g, 90 mmol) and 18-crown-6 (0.91 g, 3.4 mmol) were mechanically stirred in anhydrous THF (400 mL) at 0 ^oC under N_2 and potassium *tert*-butoxide (9.18 g, 90 mmol) was added in seven portions. The mixture was vigorously stirred for 30 min and then bis(2-bromoethyl)ether (6.9 g, 30 mmol) was added dropwise. The mixture was stirred for 7 d at room temperature (21 ^oC). The reaction solution was filtered, and THF was subsequently removed under reduced pressure. The crude product was purified via silica chromatography (ethyl acetate/hexane = 1:2, v/v) to give a colorless liquid (5.11 g, 77% yield). ^1H NMR (300 MHz, $CDCl_3$, δ,

ppm): 8.33, 8.09 (2s, 2H, -C(=O)H), 7.24, 6.59 (2m, 2H, CH_2=CH-), 4.71-4.44 (m, 4H, CH_2=CH-), 3.76 (m, 4H, -N-CH_2-), 3.59 (m, 4H, -CH_2-O-).

Polyamine Particle Synthesis. A mixture of *N*-methyl-*N*-vinylformamide (50 mg, 0.59 mmol), di[2-(*N*-vinylformamido)ethyl] ether (372 mg, 1.76 mmol), AIBN (6.0 mg, 0.037 mmol), 1-propanol (3.75 mL), and water (2.25 mL) was bubbled with nitrogen for 5 min under mechancal stirring at 300 rpm. This mixture was heated to 60 ^{o}C and held at that temperature for 12 h before more AIBN (6.0 mg, 0.037 mmol) was added and the resultant mixture was heated at 70 ^{o}C, 80 ^{o}C, and then 90 ^{o}C for 1 h at each temperature, respectively. The final particles were settled by centrifugation and seperated from the supernatant. They were re-dispersed in 20 mL of water by stirring and settled by centrifugation. This rinsing step was repeated twice using water as the solvent and then rinsed twice more using methanol as the solvent. The particles were subsequently cleaned by Soxhlet extraction with water (100 mL) overnight.

Particles in concentrated HCl (20 mL) were refluxed for 3 d. The solution was centrifuged and the solid was washed with water until the supernatant was neutral. The solid was re-dispersed into a 2 M NaOH solution (100 mL) and heated at 80 ^{o}C for 16 h. The final polyamine particles were settled by centrifugation, separated from the supernatant, and redispersed in 40 mL of water. This particle settling and supernatant removal procedure was repeated 8 times before the particles were dried under vacuum at 50 ^{o}C overnight to produce 196 mg of solid (63% yield based on full incorporation of monomer and crosslinker and full deprotection of the amine groups).

Titration of Accessible Amine Groups. Stock solutions of aqueous HCl (0.100 M, 100 mL) and aqueous NaOH (0.0503 M, 100 mL) were prepared and standardized. Polymer particles (41.3 mg) were stirred in the HCl solution (10 mL) for 24 h to neutralize the accessible amine groups. After particle settlement by centrifugation, the supernatant was collected. The polymer particles were washed with distilled water (3×10 mL) and all of the washing solutions were subsequently combined. The supernatant containing unreacted HCl was titrated with the NaOH solution and the pH change of the system was monitored using a pH meter. From the titration curve, the residual HCl amount was determined, and this allowed the calculation of the quantity of accessible amines in the particles. The accessible amine determination was repeated and the reported value was the average of these two experiments.

CO_2 Adsorption and Desorption. A Mettler Toledo (model: ML204/03, d = 0.1 mg) analytical balance was used to measure the quantity of absorbed CO_2 by the polyamine particles. The CO_2 flow was maintained at approximately 30 cm^3/min. Sand (Fischer Scientific) was placed in a vial and exposed to a CO_2 atmosphere for an hour and this control experiment demonstrated that sand did not contribute to CO_2 capture. A sample of polyamine particles (511.4 mg), was covered with sand (2.5 g) in a 1.5 mL vial (with a screw cap containing a rubber septum), and activated at 80 ^oC under vacuum overnight before analysis. The polyamine particles at the bottom of the vial were slowly stirred. A long needle, connected with gas (CO_2 for the sorption or N_2 for the desorption) was inserted into the vial containing the polyamine particles. Another short needle was passed through the septum of the cap and used to allow the excess gas to escape the vial. A

water bath was used because water can be quickly dried with a paper towel so that the weight difference by an analytical balance could be obtained conveniently. The gas flow was kept at each temperature for 30 min. When the desorption experiment was carried out, the inlet gas was switched to N_2 and the vial was heated at 100 ^oC for 30 min. After cooled down to room temperature, the total weight was almost the same as that before the vial was connected with CO_2 flow.

Isothermal CO_2 Adsorption under Various Partial Pressures. In order to control the partial pressure of CO_2, N_2 and CO_2 flows were controlled by separate regulators and measured using an Intelligent Digital Flowmeter (Varian Analytical Instruments). Once both of the flow rates were stable, two long steel needles were connected to the N_2 and CO_2 gas cylinders (one needle was used for each gas source) and inserted into a rubber septum covering a flask where the two gases were mixed at room temperature. A helical hollow steel tube was also connected to this flask through septum, and this tube led to a test vial similar to that used for the adsorption and desorption experiments. Both the helical steel tube and the test vial were immersed in water baths that were both maintained at the same temperature to control the temperature of the gas mixture. The total flow rate of the gas mixture was 300 mL/min. Using this device and this procedure, we hoped that the partial pressure of CO_2 in the mixture was given by the ratio between the flow rate of CO_2 and that of the gas mixture.

The isothermal sorption determination experiment began at the lowest partial pressure of CO_2 (around 0.10 atm) and the highest partial pressure of N_2 (around 0.90 atm) employed,

and each partial pressure was maintained for 100 min. Subsequently, the partial pressure of CO_2 was gradually increased while that of N_2 was decreased, and the new partial pressures were maintained for 100 min before the next incremental partial pressure change.

To ensure that this gas mixing protocol would yield gas mixtures with the targeted partial pressures, the gas mixture was passed through an aqueous NaOH solution (0.104 M, 200 mL). The times required to reduce the pH of the NaOH solution to 8.30 were recorded. This pH was chosen because the carbonic acid would be fully converted to $NaHCO_3$ by this pH. Plotted in Figure S6 is the variation in the inverse flow time as a function of the ratio between the CO_2 flow rate and the total gas flow rate. Since the total flow rate was constant at 150 mL/min and the total gas pressure was constant at 1.00, the partial pressures of CO_2 in the gas mixtures had to be equal to the gas flow rate ratios.

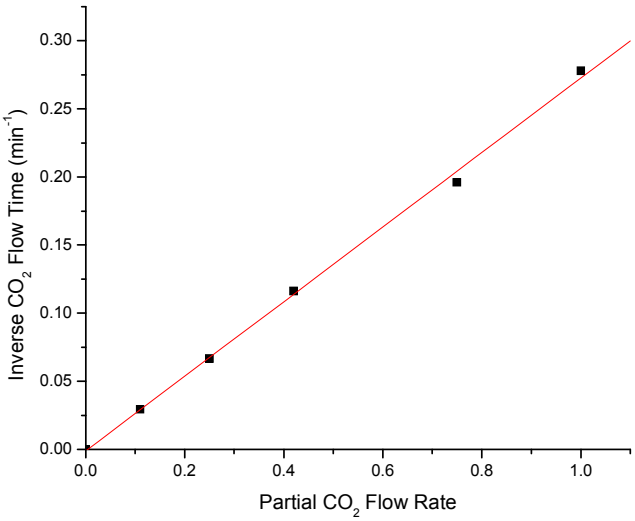

Figure S6. Variation in the inverse of the flow time required to reduce the pH of 200 mL of an aqueous 0.104 M NaOH solution to 8.30 at room temperature as a function of the

relative rate of CO_2 flow for CO_2 and N_2 mixtures flowing at a total flow rate of 150 mL/min.

The total flow rate used in the titration experiment was lower than 300 mL/min used in the isothermal experiment because we wanted to ensure that CO_2 was fully reacted with NaOH. This was to ensure by passing the gas through a frit so that small bubbles were generated. Also, the NaOH solution was contained in a slim cylindrical tube that was filled in the top 90% section by glass wool so that the path of CO_2 in the basic solution was long and tortuous. The mixing was further facilitated by stirring the solution vigorously.

A straight line should be obtained when $1/t$ was plotted vs. p_{CO2} because p_{CO2}v should be a constant. Here v is the total volume of gas passing through the NaOH solution and is equal to flow rate times flow time *t*.

Specific Surface Area Measurements. A polyamine particle sample was degassed at 140 ^{o}C for 4 h. A nitrogen sorption isotherm was run on a Quantachrome Autosorb-1C at 77 K. Five points starting at $P/P_o = 0.1$ were selected and the specific surface area was calculated using the BET method.

Multi-point BET data:

Relative Pressure (P/P_o)	Volume @ STP (cc/g)	$1 / [W((P_o/P) - 1)]$
0.101027	67.4450	1.3332
0.157375	78.3362	1.9076

0.207897	84.7842	2.4769
0.257741	90.8232	3.0590
0.307317	96.9495	3.6615

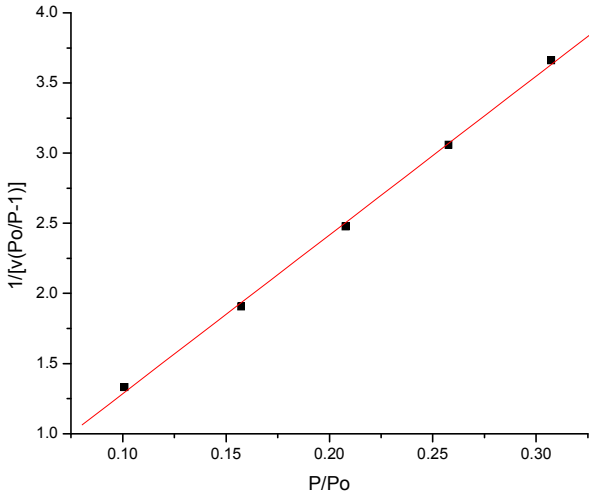

Figure S7. N_2-sorption isotherm of the obtained polyvinylamine particles (Slope = 11.313; Intercept = 0.154; Correlation coefficient, r = 0.999415; C constant = 74.427)

$$V_m = \frac{1}{\text{slope} + \text{intercept}} = \frac{1}{11.313 + 0.1541} = 0.0872$$

$$S_t = \frac{V_m L_{AV} A_m}{M_v} = \frac{0.0872 \times (6.022 \times 10^{23}) \times (0.162 \times 10^{-18})}{\frac{28}{0.808}} = 246\ m^2/g$$

Note: V_m represents the monolayer capacity, $1/M_v$ represents the molar volume, L_{av} is Avogadro′s number, and A_m is the cross-sectional area.[i]

[i] S. Brunauer, P. H. Emmett, E. Teller, *J. Am. Chem. Soc.* **1938**, *60*, 309.