Electronic Supplementary Information (ESI) for:

Direct air capture (DAC) of CO₂ using Polyethylenimine (PEI) “Snow”: A scalable strategy

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Experimental section

Materials

All chemicals are purchased from commercial sources and are used as supplied. Branched polyethylenimine (PEI) with a weight-average molecular weight of ~25,000 (purity ≥ 99%), triglycidyl trimethylolpropane ether (TTE, technical grade), methanol (purity ≥ 99.8%), and ethanol (reagent grade) were supplied by Sigma-Aldrich. High purity N₂ (99.9%) was the product of BOC Gas. Distilled water was always used in the preparation of PEI solutions.

Synthesis of PEI snow

9.0 g of PEI~25,000 aqueous solution with mass concentration of 30.0 wt.% was added into a 20 mL plastic sample vial. Subsequently, varying amounts of TTE were dissolved into 1.0 g of methanol to prepare methanol solutions with different TTE concentrations. The two solutions were then mixed up and manually shaken to initiate the PEI crosslinking reaction at the ambient temperature. The crosslinking reaction terminated within 15 min depending on the cross-linker (TTE) concentration and eventually a bulk PEI gel was produced. Afterward, the PEI gel was vigorously ground using a glass stirring rod to obtain a snow-like material that had an average particle size of 200 ~ 300 µm. The powdery material was then rinsed by excessive amount of ethanol and distilled water to remove the solvent methanol that would affect the measurement of δ¹³C-CO₂ by the Isotopic Analyzer. To maintain the same PEI concentration, we weighed the sample prior to the rinsing, and then placed the water-saturated sample in a fume cupboard to dry it and weighed it every 30 min. Considering that the amounts of unreacted TTE and solvent ethanol were insignificant, we reckoned the PEI concentration was nearly the same (i.e. 30 wt.%) if the dried sample weight equalled to the original weight (before rinsing), and the drying process was terminated. It was noted that this material product was used as prepared for the subsequent characterizations and DAC measurements without pre-treated or dried, and they are virtually “dry”.
**Infrared Spectroscopy of PEI crosslinking reaction**

To validate the occurrence of crosslinking reaction between PEI and TTE, mid-infrared spectroscopy measurements were made using a Vertex-70 FTIR spectrometer (Bruker) equipped with a DLaTGS detector. Data was recorded between 4000 ~ 400 cm\(^{-1}\) at a resolution of 2 cm\(^{-1}\) and 32 scans were averaged for each spectrum. Prior to any measurements, the surface of the ATR was cleaned with water and ethanol and wiped with laboratory cleaning tissue (Kimwipe). A new background was then recorded. PEI aqueous solution and TTE methanol solution were mixed up in a sample vial at room temperature. One tiny drop of the mixture was quickly placed on the ATR surface and the IR measurement lasted for 20 min. All experiments were conducted at ambient temperature (20 ± 2°C).

**Infrared Spectroscopy of CO\(_2\) absorption by PEI snow**

The Vertex-70 FTIR spectrometer (Bruker) equipped with a DLaTGS detector was also employed for the conformation of CO\(_2\) absorption by PEI snow. Instead of the ATR diamond, a Pike Technologies Horizontal Attenuated Total Reflectance (HATR) accessory was used with a trough type ZnSe ATR plate. About 1g of PEI snow was placed onto the ATR plate by a sample spatula. The sample was pressed down by the top of the flow cell before the CO\(_2\) was introduced at a flow rate of 100 ml/min. The IR measurement was then initiated and continued for 45 min. All experiments were conducted at ambient temperature (20 ± 2°C).

**Thermogravimetric-Differential Scanning Calorimetry (TG-DSC) analysis**

A given amount of CO\(_2\)-saturated PEI snow was loaded into the crucible of a STD Q600 thermal analyzer. α-Al\(_2\)O\(_3\) was used as the sample reference. Afterward, the furnace was purged by nitrogen flow with a flow rate of 100 ml/min for 1 h. Subsequently, the furnace temperature was increased from room temperature to 300 °C with a heating rate of 5 °C/min in a N\(_2\) protective stream (30 ml/min). Information including the heating
temperature (°C), sample mass change (%), derivative thermo-gravimetric (%/min) and heat flow (mW/mg) as a function of time were measured and recorded automatically by the software throughout the TG-DSC experiments.

**Direct air capture of CO\textsubscript{2} by the PEI snow**

Unlike most of the reported DAC experiments which used synthetic gas as the gas source, herein we used real air in the lab to assess the DAC capacity of the PEI snow. The schematic of the experimental set-up is presented in Figure S1. Generally, the air was continuously sucked in by a compressor and was introduced into the pipeline. The air flow rate was monitored and controlled by the mass flow controller (Bronkhorst\textsuperscript{®} model F-201AV). A bubbler was installed at the inlet of the sample column to avoid the dehydration of the PEI snow caused by the gas flow. For each measurement, 15-17 g of PEI snow was loaded into the Swagelok column with a dimension of 0.5 m × 1/2". Filter papers were positioned at the inlet and outlet of the column to prevent the PEI snow contaminating the pipelines. The air with constant flow rate entered the sample column and interacted with the absorbent (PEI snow), the residual CO\textsubscript{2} concentration in the effluent gas was identified by the isotopic analyzer throughout the experiments. The total amount of the absorbed CO\textsubscript{2} can be readily determined from the breakthrough curves.\textsuperscript{1} The DAC performance of PEI snow was also examined at large scale (~ 60 g sample) using a brass column and the actual experimental set-up is shown in Figure S2.

**Regeneration of the PEI snow**

So far, nearly all the existing DAC materials are regenerated via the temperature-swing or pressure-swing methods, which will consume enormous amount of energy. To overcome this issue, we applied steaming heat which was normally treated as “waste heat” in the industry to recover the capacity of the PEI snow. The schematic set-up is illustrated in Figure S4. 15-17 g of PEI snow was loaded into the sample column for the DAC investigation. After the outlet CO\textsubscript{2} concentration equaled to the atmospheric
level, the column including the sample was taken off from the pipeline and hooked up to a water tank that was placed in a convective oven. The heating temperature was set to be 120 °C to generate the water steam that could desorb the CO₂. After 30 min, the heating was terminated and the column was cooled down to the room temperature. Subsequently, the steaming-heated column was subject to air flow again to evaluate the DAC capacity of the regenerated PEI snow. Ten absorption-desorption cycles were performed in total.

**Figure S1.** Schematic of the experimental set-up for evaluating the DAC performance of PEI snow. 1. Air compressor 2. Gas pressure gauge 3. Mass flow controller 4. Bubbler 5. Sample column 6. Isotopic analyzer
Figure S2. Experimental set-up for evaluating the DAC performance of PEI snow at relatively large scale.

Figure S3. Appearance and rigidity of PEI snow with (a) 3.0 wt. %, (b) 6.0 wt. % of TTE. It was clear that higher levels of TTE could boost the powdery nature and increase the dryness of the PEI snow.
Figure S4. Schematic set-up of the PEI snow regeneration via steam heating at 120 °C.

Figure S5. Absorption curves of first, fifth and last regeneration cycles. These curves were highly overlapped, indicating that the CO$_2$ could be completely desorbed in each cycle and that DAC capacity of PEI snow was hardly compromised by the steaming heat.
Figure S6. IR spectrum of the CO$_2$ absorption and desorption by PEI snow in multiple cycles. The pristine PEI snow was first scanned by the IR (indicated as “Start”). After the CO$_2$ absorption in the first cycle (indicated as “1$^{st}$ absorption”), a few new peaks appeared, demonstrating the effective CO$_2$ absorption. Then the CO$_2$-loaded sample was subject to the steaming heat and it was found the IR peaks nearly overlapped that of the pristine sample. The fifth cycle repeated the same trend. After the steaming heat in the tenth cycle (indicated as “Finish”), it was seen that no new peaks appeared, demonstrating that the chemical structure of PEI snow was hardly affected by the steaming heat because no thermal and oxidative degradation occurred in ten cycles.

Figure S7. DAC capacities of various types of adsorbents/absorbents (25 °C, CO$_2$ 400 ppm). HAS and TRI-PE-MCM-41 are supported amine sorbents. SWCNT is a carbon nanomaterial. PPN-6-CH2 is a microporous organic polymer (MOP), SIFSIX-3-Cu and
M2(dobpdc) are metal organic frameworks (MOFs).

Figure S8. DAC performance of PEI snow at bench scale. The main inputs and outputs of the experimental were inserted in the graph. The CO$_2$ uptake was identified to be 63.02 mg CO$_2$/g absorbent, which was outstanding considering the applied sample weight and the flow rate.

References


