Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Material

for

Capture and conversion of carbon dioxide by solar heat localization

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Materials

1-Methylimidazole, 3-(perfluorooctyl) propyl iodide, and dry acetonitrile were obtained from Sigma Aldrich, while bis(perfluoroethylsulfonyl)amide lithium salt was obtained from TCI chemicals. The ionic liquids (ILs), C10MI·BF_4 and C16MI·Tf_2N, were obtained from Ionic liquid technologies.

Synthesis Procedures

Preparation of Graphene Aerogel (GA)

Graphene aerogel was synthesized using a previously reported method.[1] A 100 mg portion of L-phenylalanine was dissolved in 5 mL of distilled water. Once dissolved, 5 mL of graphene oxide was added, and the solution was poured into a 25 mL vial for sonication (10 min). After sonication, the solution was placed in a hot oil bath at 95 °C for 48 hours to yield a wet hydrogel. The hydrogel was freeze dried for 48 hours at ~65 °C to obtain the graphene aerogel (GA). An optical image of the GA is shown in **Fig. S1**.

Fig. S1. Optical image of the synthesized graphene aerogel (GA).

Ionic Liquids

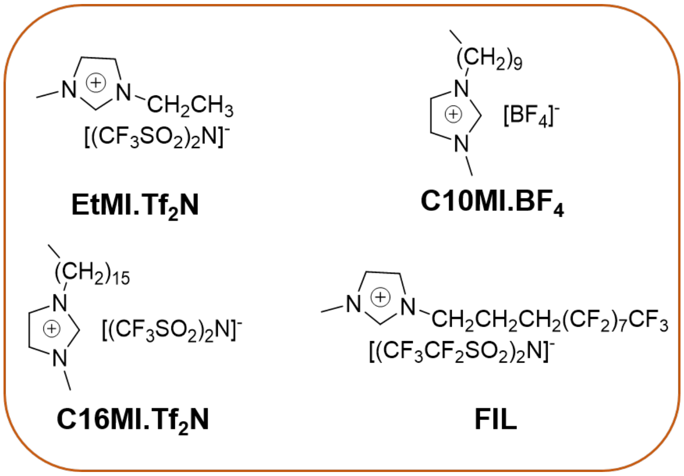
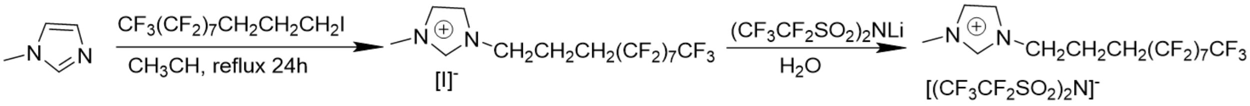


Fig. S2. Structures of the ionic liquids used. EtMI.Tf$_2$N was used for benchmark experiments. C10MI.BF$_4$, C16MI.Tf$_2$N and FIL were tested for CO$_2$ capture in the SCCs.

Synthesis of the fluorinated ionic liquid (FIL):[2] 1-(3-perfluorooctyl) propyl-3-methylimidazolium bis(perfluoroethylsulfonyl) amide



1

2

1-Methylimidazole (8.5 mmol) and 3-(perfluorooctyl) propyl iodide (8.5 mmol) were dissolved in 20 mL of dry acetonitrile and refluxed for 24 hours. After cooling to room temperature, the resulting mixture was washed with diethyl ether and filtered. The resulting residue was dried in a vacuum oven to give 1-(3-perfluorooctyl) propyl-3-methylimidazolium iodide (**1** from the scheme shown above) as a white powder in 85 % yield. ^{1}H NMR (JOEL ECX-600, DMSO-d$_6$, 600 MHz, δ, ppm): 9.07 (N–***CH***–N, s, 1H), 7.78 (N–***CH***–CH, d, 1H), 7.69 (N–***CH***–CH, d, 1H), 4.24 (N–***CH$_2$***, t, 2H), 3.81 (N–***CH$_3$***, s, 3H), 2.46 (N–CH$_2$–***CH$_2$***, m, 2H), 2.06 (N–CH$_2$–CH$_2$–***CH$_2$***–(CF$_2$)$_7$CF$_3$, m, 2H). ^{19}F NMR (JOEL ECX-600, DMSO-d$_6$, 600 MHz, δ, ppm): -80.09 (***CF$_3$***, t, 3F), -113.13 (CF$_3$–***(CF$_2$)$_7$***–CH$_2$, q, 2F), -121.46 (CF$_3$–***(CF$_2$)$_7$***–CH$_2$, d, 6F), -122.40 (CF$_3$–***(CF$_2$)$_7$***–CH$_2$, s, 2F), -122.84 (CF$_3$–***(CF$_2$)$_7$***–CH$_2$, s, 2F), -125.66 (CF$_3$–***(CF$_2$)$_7$***–CH$_2$, s, 2F).

1-(3-Perfluorooctyl)propyl-3-methylimidazolium iodide (2.2 mmol) was then dispersed into 50 mL of water. Bis(perfluoroethylsulfonyl)amide lithium salt (2.5 mmol) was slowly added to the solution with vigorous stirring. The mixture was stirred at rt for 24 hours. Afterward, the resulting precipitate was filtered out and was washed with water (3 × 100 ml). The resulting 1-(3-perfluorooctyl) propyl-3-methylimidazolium bis(perfluoroethylsulfonyl) amide (FIL, **2** from scheme) was dried in a vacuum oven and obtained in 80% yield. ^{1}H NMR (JOEL ECX-600, DMSO-d_6, 600 MHz, δ, ppm): 9.07 (N–$\boldsymbol{CH}$–N, s, 1H), 7.77 (N–$\boldsymbol{CH}$–CH, d, 1H), 7.60 (N–$\boldsymbol{CH}$–CH, d, 1H), 4.25 (N–$\boldsymbol{CH_2}$, t, 2H), 3.83 (N–$\boldsymbol{CH_3}$, s, 3H), 2.31 (N–CH_2–$\boldsymbol{CH_2}$, m, 2H), 2.09 (N–CH_2–CH_2–$\boldsymbol{CH_2}$–$(CF_2)_7CF_3$, m, 2H). ^{19}F NMR (JOEL ECX-500, DMSO-d_6, 500 MHz, δ, ppm): -78.52 ($\boldsymbol{CF_3}$–CF_2–SO_2, t, 6F), -80.14 ($\boldsymbol{CF_3}$, 3F), -117.36 (CF_3–$\boldsymbol{CF_2}$–SO_2, s, 4F), -113.15 (CF_3–$\boldsymbol{(CF_2)_7}$–CH_2, t, 2F), -121.45 (CF_3–$\boldsymbol{(CF_2)_7}$–CH_2, d, 6F), -121.40 (CF_3–$\boldsymbol{(CF_2)_7}$–CH_2, s, 2F), -122.83 (CF_3–$\boldsymbol{(CF_2)_7}$–CH_2, s, 2F), -125.66 (CF_3–$\boldsymbol{(CF_2)_7}$–CH_2, s, 2F).

Preparation of the SCC

To integrate the synthesized FIL with GA, the FIL was heated on a heater to ~70 °C, which is above its melting point (56 °C). Once the FIL was observed to undergo a solid-liquid phase change, the GA was placed on the melted FIL. The GA being highly oleophilic, absorbed the FIL completely. Next, the GA-IL composite was allowed to cool at room temperature to form the SCC.

Assignment of the Major Peaks in the FT-IR Spectra in Figure 4

The peak at 1150 cm^{-1} is due to the C-F stretches observed for FIL and C16MI.Tf_2N, the peak at 1570 cm^{-1} presents imidazolium ring stretch, and the peak at 1325 cm^{-1} shows aromatic tertiary amine C-N stretch. Peaks at 2865 cm^{-1} and 2935 cm^{-1} are assigned to methylene C-H symmetric and asymmetric stretch.[3–5]

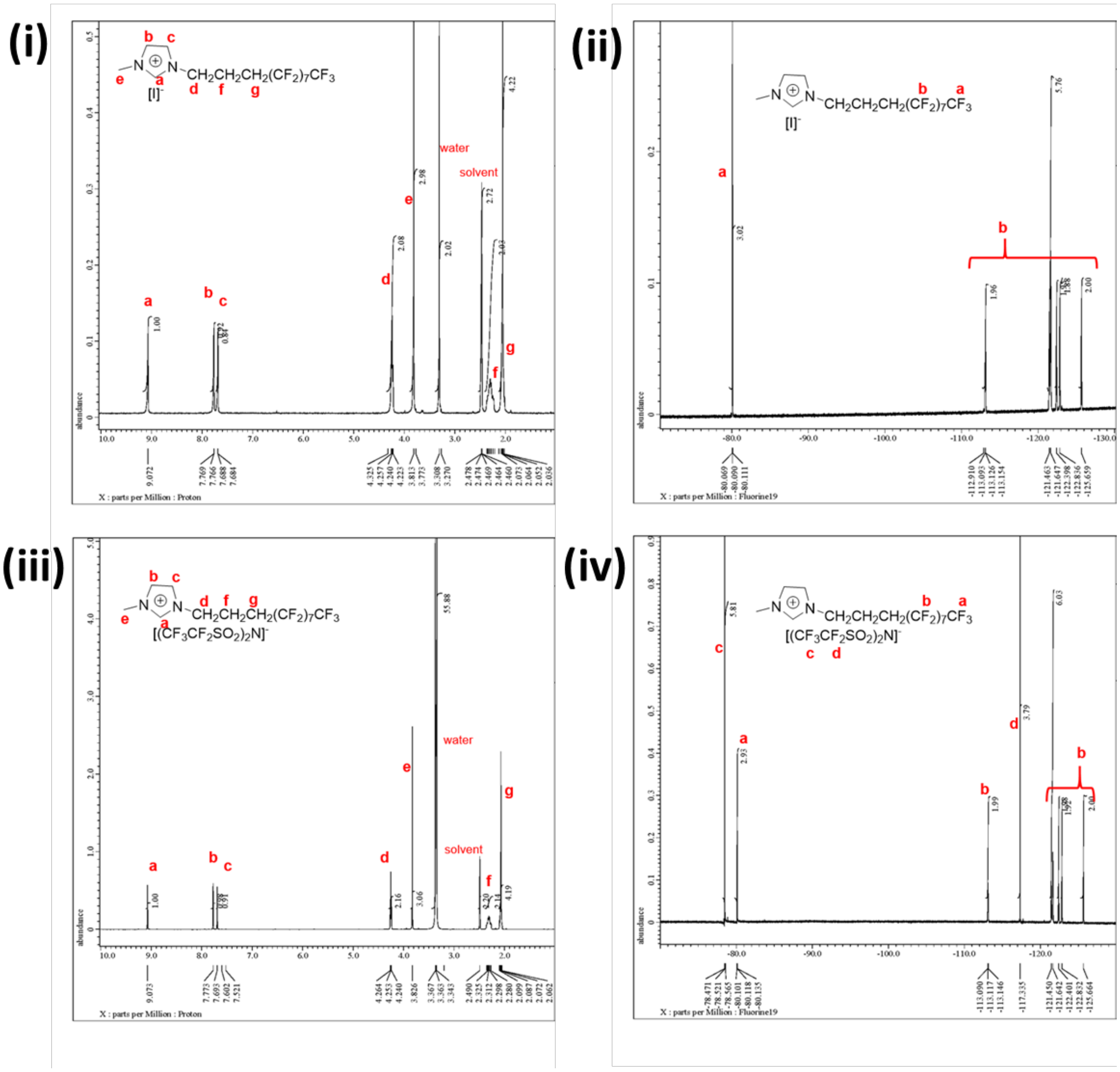


Fig. S3. NMR spectra: (i) ^{1}H NMR spectrum of 1-(3-perfluorooctyl) propyl-3-methylimidazolium iodide, **1**; (ii) ^{19}F NMR spectrum of 1-(3-perfluorooctyl) propyl-3-methylimidazolium iodide, 1; (iii) ^{1}H NMR spectrum of 1-(3-perfluorooctyl) propyl-3-methylimidazolium bis(perfluoroethylsulfonyl) amide (FIL), **2**; (iv) ^{19}F NMR spectrum of 1-(3-perfluorooctyl) propyl-3-methylimidazolium bis(perfluoroethylsulfonyl) amide (FIL), **2.**

Experimental Setups

Mole Fraction of CO_2 Absorbed (Pressure Drop Experiment)

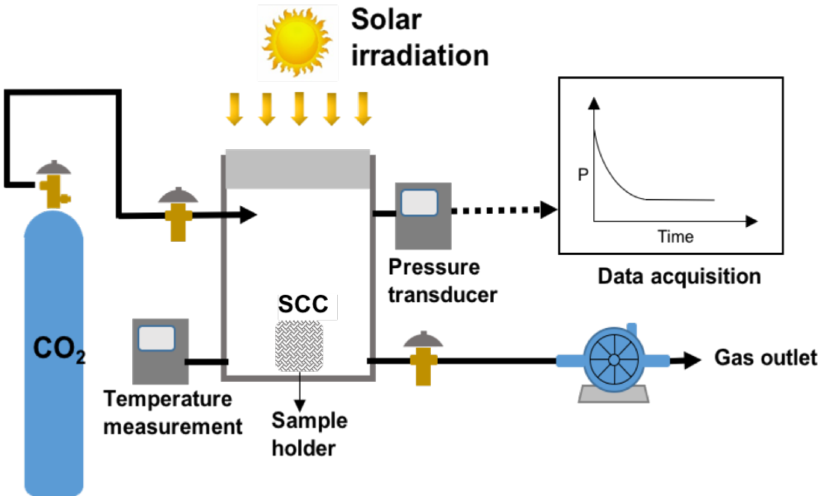


Fig. S4. Schematic illustration of the experimental setup used for the pressure drop experiments.

A custom setup was designed to capture CO_2 with solar illumination, as shown in **Fig. S4**. The SCC was placed into an acrylic sample holder in a cylindrical chamber of 25.4 mm diameter with a glass flange attached on top. The chamber was designed with an input and an output. The chamber was equipped with a thermocouple and the setup was placed under a solar illuminator (OAI 0131-0293-01 with Aluminum mirror and 1.6 kW lamp) until the temperature reached a constant value above the melting point of the ionic liquid. The pressure in the chamber was monitored using a pressure transducer (Prosense, SPT25-20- 0500A). The thermocouple and the pressure transducer were connected to the data acquisition system, and the generated data was collected by a LabView program. The pressure was maintained between 2 bar and 6 bar and a temperature of 25 °C for ~40 minutes in the cylindrical chamber during each experiment. The amount of CO_2 captured (in terms of mole fraction) was then calculated using the observed drop in pressure using the ideal gas equation.

CO_2 Concentration in Gas Mixture Using a Gas Analyzer

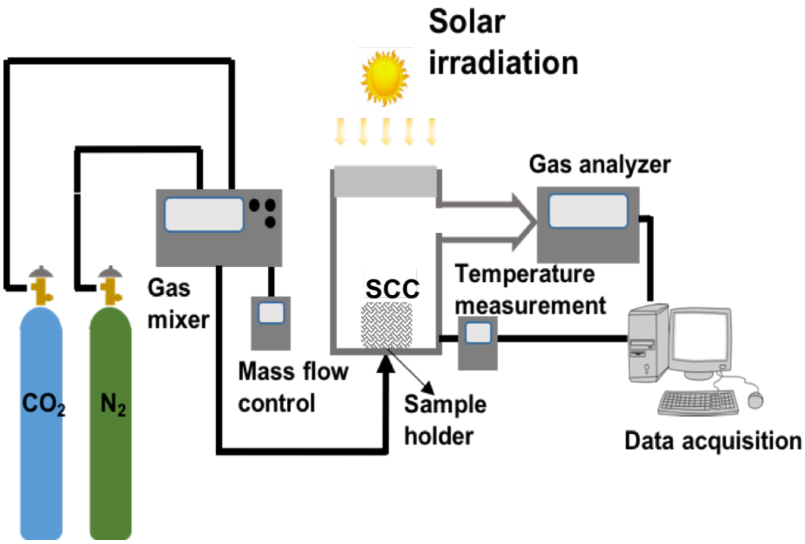


Fig. S5. A schematic of the experimental setup to verify the capture of CO_2 from a gas mixture using a gas analyzer.

An experimental setup was designed as shown in **Fig. S5** to quantify the amount of CO_2 absorbed in the SCCs. A known mass and mixture of nitrogen and CO_2 gas was prepared using a gas mixer (Wittgas KM-20) and passed through the SCC samples at a known pressure and temperature (25 °C). Note that the gas mixture was maintained inside the pressure cylinder at a pressure between 2 and 6 bar. Solar irradiation of 1 kWm^{-2} was passed onto the SCC samples. The output gas was analyzed using a gas analyzer (Wittgas PA 7.0), which was connected to a data acquisition system provided with the device, to determine the percentage drop of CO_2. The temperature of the sample was also monitored constantly to evaluate the temperature for phase change.

NMR After CO_2 Capture

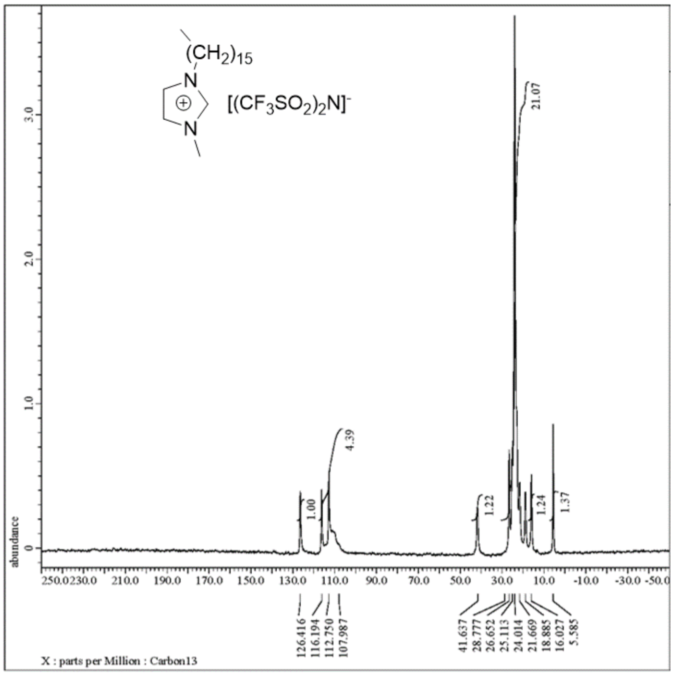


Fig. S6. NMR measurements for C16MI.Tf_2N before CO_2 capture is shown.

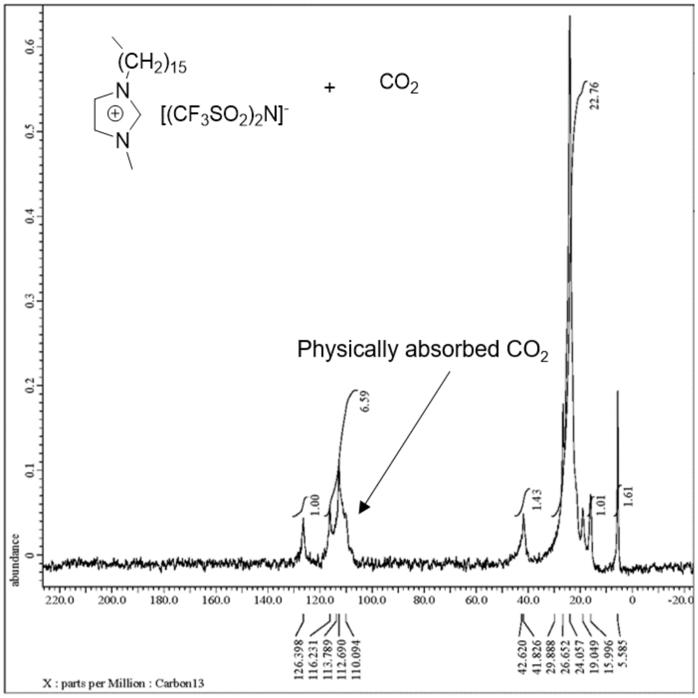


Fig. S7. NMR measurements for C16MI.Tf_2N after CO_2 capture is shown.

Involved Chemical Reactions for the Washing Process

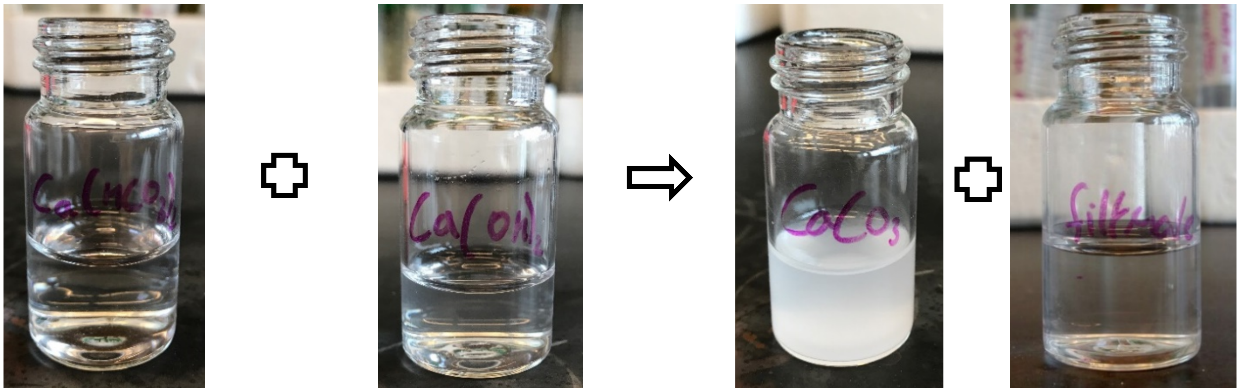
$$Ca(OH)_2\ (aq) + CO_2\ (g) \rightarrow CaCO_3\ (s) + H_2O\ (l) \tag{1}$$

$$CaCO_3\ (s) + CO_2\ (g) + H_2O\ (l) \rightleftharpoons Ca(HCO_3)_2\ (aq) \tag{2}$$

$$Ca(OH)_2\ (aq) + 2CO_2\ (g) \rightleftharpoons Ca(HCO_3)_2\ (aq) \tag{(1) + (2)}$$

$$Ca(HCO_3)_2\ (aq) + Ca(OH)_2\ (aq) \rightleftharpoons 2CaCO_3\ (s) + 2H_2O\ (l) \tag{3}$$

Alternate Method for Precipitation of $CaCO_3$



$Ca(HCO_3)_2$ Low conc. $Ca(OH)_2$ $CaCO_3$ filtrate

Fig. S8. Optical images for the precipitation of $CaCO_3$.

Experimental setup for continuous operation of SCC

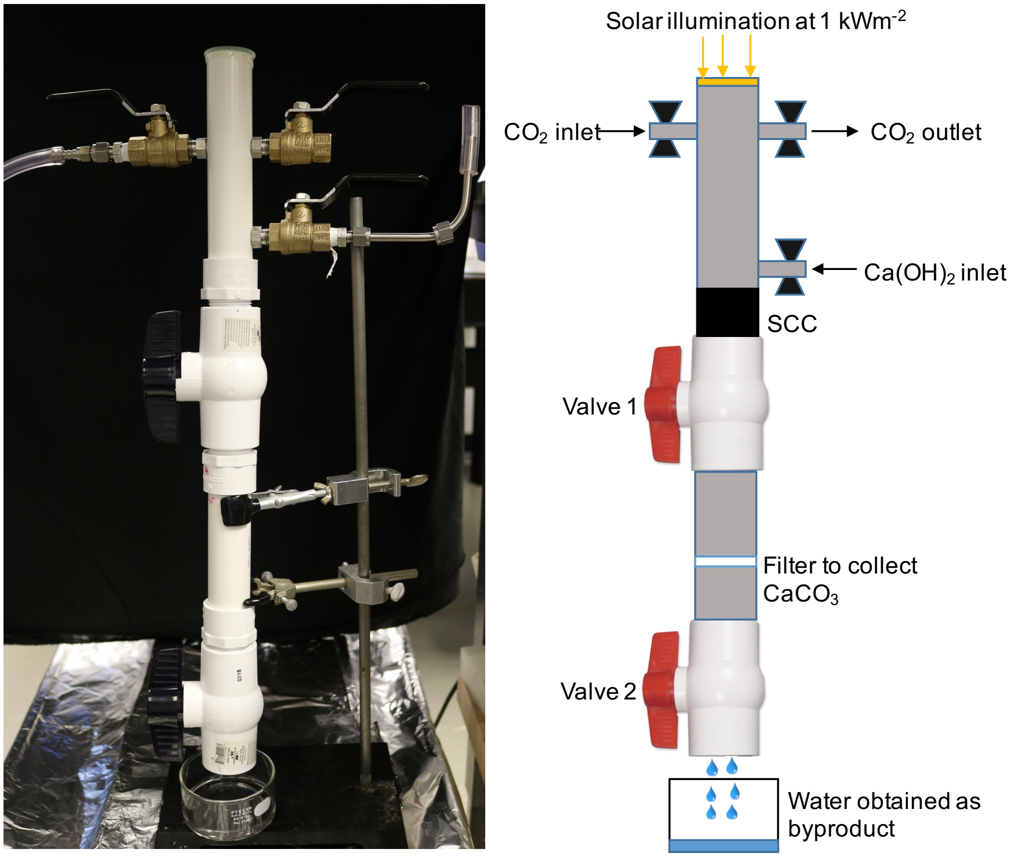


Fig. S9. Schematic of the experimental setup to demonstrate the continuous operation of SCC. Here, CO_2 was captured at 2 bar pressure by SCC, and byproducts including water and $CaCO_3$ were obtained.

A prototype was developed in the Nanotherm laboratory to demonstrate continuous operation of SCC for CO_2 capture while producing water and $CaCO_3$ as shown in **Fig. S9**. Note that PVC was used in the fabrication of this system in order to ensure cost effectiveness for large scale operation. Valves are provided for the inlet and outlet of CO_2 gas and also for inlet of $Ca(OH)_2$ solution. SCC was placed inside the system just below the $Ca(OH)_2$ inlet as shown in the schematic. CO_2 gas at 2 bar pressure was passed and the system was pressurized. Once SCC captured the CO_2 gas, the system was depressurized and SCC was washed with $Ca(OH)_2$ solution. Valve 1 from the schematic was kept closed to allow for the formation of $CaCO_3$. Valve 1 is then opened to allow for the $CaCO_3$ to be filtered using a filter placed in the system. Once the $CaCO_3$ is filtered, water is collected by opening valve 2. A video demonstration for the continuous operation of SCC is attached with the supplementary materials as **Movie S1**.

Washing partially miscible SCC(C10MI.BF_4) with 0.01M $Ca(OH)_2$

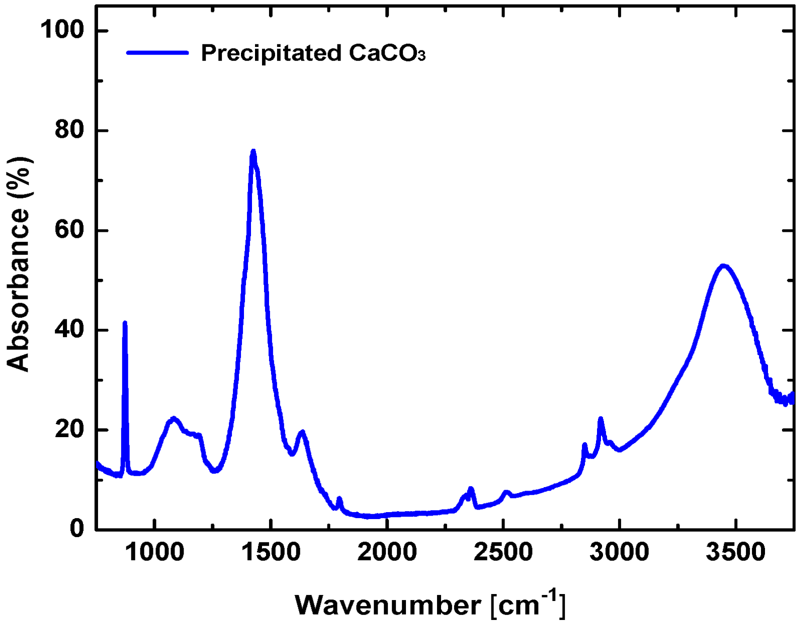


Fig. S10. FTIR spectrum of precipitated $CaCO_3$ (obtained by washing SCC(C10MI.BF_4)

Movie S1.

Demonstration of the system prototype

References

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