Capturing carbon dioxide as a polymer from natural gas

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Natural gas is considered the cleanest and recently the most abundant fossil fuel source, yet when it is extracted from wells, it often contains 10–20 mol% carbon dioxide (20–40 wt%), which is generally vented to the atmosphere. Efforts are underway to contain this carbon dioxide at the well-head using inexpensive and non-corrosive methods. Here we report nucleophilic porous carbons are synthesized from simple and inexpensive carbon–sulphur and carbon–nitrogen precursors. Infrared, Raman and 13C nuclear magnetic resonance signatures substantiate carbon dioxide fixation by polymerization in the carbon channels to form poly(CO2) under much lower pressures than previously required. This growing chemisorbed sulphur- or nitrogen-atom-initiated poly(CO2) chain further displaces physisorbed hydrocarbon, providing a continuous carbon dioxide selectivity. Once returned to ambient conditions, the poly(CO2) spontaneously depolymerizes, leading to a sorbent that can be easily regenerated without the thermal energy input that is required for traditional sorbents.
An automobile operating on natural gas produces ~30% lower carbon dioxide (CO$_2$) emissions than when operating on gasoline. Provided technological efficiencies are maintained to minimize direct natural gas leakage to the atmosphere, there is a significant lowering of greenhouse gas emissions when using natural gas rather than liquid hydrocarbons. At the same time, natural gas wells have typical CO$_2$ concentrations of 10–20 mol%, and that can rise to as high as 70 mol% in some locations. The CO$_2$ is generally vented into the atmosphere at natural gas collection stations, significantly offsetting the environmental advantages of using natural gas as a fuel. Typically, aqueous amine scrubbers are used to remove CO$_2$ from natural gas, but aqueous amines are corrosive, and the CO$_2$-containing liquid requires heating to 125–140 °C to liberate the CO$_2$ from the amine carbonate. This heating demands a high energy input and the scrubbers are not easily amenable to offshore CO$_2$ capture due to their size and weight. Long and other groups extensively reviewed aqueous amines and other methods of CO$_2$ capture that include metal oxide frameworks, zeolites, ionic liquids, cryogenic distillation, membranes and metal oxides. Some of these have hydrolytic instabilities and/or low densities leading to low volumetric efficiencies, or sometimes poor selectivity relative to methane, but most often there are synthesis constraints or energy costs associated with these technologies that lessen their suitability for on-site CO$_2$ capture from natural gas.

Here we report new materials from simple and inexpensive carbon–sulphur or carbon–nitrogen solid sorbents, which separate CO$_2$ from natural gas, with 0.82 g CO$_2$ per g of sorbent (82 wt%) captured at 30 bar. A mechanism is described where CO$_2$ is polymerized in the channels of the support, as initiated by the sulphur or nitrogen atoms that are part of the carbon framework. No temperature swing is needed; it proceeds at ambient temperature. Eventually, heat transfer between cylinders during the exothermic sorption and endothermic desorption might provide the requisite thermodynamic exchanges. The process uses the inherent natural gas-well pressure of 200–300 bar as a driving force during the polymerization. By lowering the pressure back to ambient conditions after CO$_2$ uptake, the poly(CO$_2$) then depolymerizes where it can be off-loaded, or pumped back downhole into the structures that had held it for geological timeframes.

**Results**

**Synthesis and characterization of porous carbons.** Sulphur- and nitrogen-containing porous carbons (SPC and NPC, respectively) were prepared by treating bulk precursor polymers with potassium hydroxide (KOH) at 600 °C (Fig. 1a; refs 10,11). The resulting products were solid porous carbon materials with homogeneously distributed sulphur or nitrogen atoms incorporated into the carbon framework. They exhibited pores and channel structures as well as high surface areas of 2,500 and 1,490 m$^2$/C$_0$ (N$_2$, Brunauer–Emmett–Teller) for the SPC and the NPC, respectively, with pore volumes of 1.01 cm$^3$/C$_0$ and 1.40 cm$^3$/C$_0$, respectively. The scanning electron microscopy and transmission electron microscopy (TEM) images are shown in Fig. 1b–d, and the X-ray photoelectron spectroscopy (XPS) analyses are shown in Supplementary Fig. 1.

**CO$_2$ uptake measurements.** Although CO$_2$ has no liquid state at ambient conditions, it can easily liquefy when the system pressure is higher, which can cause a serious analytical error during the measurements. Since there are presently no accepted standards for CO$_2$ uptake measurements, further verification was sought: the same samples were analysed using different volumetric analysis instruments at Rice University and at the National Institute of Standards and Technology (NIST), and these were further confirmed with gravimetric measurements.

Figure 2 shows the pressure-dependent CO$_2$ excess uptake for the SPC sorbent at different temperatures peaking at 18.6 mmol CO$_2$ per g of sorbent (82 wt%) when at 22 °C and 30 bar. The sorption results measured by volumetric and gravimetric analyses were comparable, as were those measurements on the two volumetric instruments. We chose 30 bar as the upper pressure limit in our experiments because a 300-bar well-head pressure at 10 mol% CO$_2$ concentration would have a CO$_2$ partial pressure of 30 bar. Figure 2b–d shows three consecutive CO$_2$ sorption–desorption cycles on SPC over a pressure range from 0 to 30 bar, which indicates that the SPC could be regenerated using a pressure swing process while retaining its original CO$_2$ sorption capacity.

In the case of microporous materials with negligible external surface area, total uptake is often used as an approximation for absolute uptake, and the two values here are within 10% of each other; for example, the absolute CO$_2$ uptake of the SPC was 20.1 and 13.9 mmol g$^{-1}$ under 30 bar at 22 °C and 50 °C, respectively (Supplementary Figs 2 and 3 and Supplementary Note 1). Similarly, although absolute adsorption isotherms can be used to determine the heat of sorption, excess adsorption isotherms are more often used to calculate the heat of CO$_2$ sorption (Q$_{CO2}$) before the critical point of the gas. Thus, the excess CO$_2$ sorption isotherms measured at two different temperatures, 23 °C and 50 °C (Fig. 2e), were input into the Claisius–Clapeyron equation (see Supplementary Note 2). At lower surface coverage (< 1 bar), which could be expected to be more indicative of the sorbate–sorbent interaction, the SPC exhibits a heat of CO$_2$ sorption of 57.8 kJ mol$^{-1}$. Likewise, the maximum Q$_{CO2}$ values for nucleophile-free porous materials, such as activated carbon, Zeolite 5 A and zeolitic imidazolate framework (ZIF-8, a class of the metal oxide frameworks) were measured to be 28.4, 31.2 and 25.6 kJ mol$^{-1}$, respectively, at low surface coverage (see Supplementary Table 1). Based on this data, the SPC possesses the highest CO$_2$ sorption enthalpy among these complementary sorbents measured at low surface coverage.

**Discussion**

In order to better assess the sorption mechanism during the CO$_2$ uptake, attenuated total reflectance infrared spectroscopy...
(ATR-IR) was used to characterize the properties of the sorbents before and after the CO2 uptake. A sample vial with ~100 mg of the SPC was loaded into a 0.8 l stainless steel autoclave equipped with a pressure gauge and valves. Before the autoclave was sealed, the chamber was flushed with CO2 (99.99%) to remove residual air, and the system was pressurized to 10 bar (line pressure limitation). The sorbent was therefore isobarically exposed to CO2 in the closed system at 23 °C. After 15 min, the system was vented to nitrogen at ambient pressure and the sorbent vial was immediately removed from the chamber and the sorbent underwent ATR-IR and Raman analyses in air.

Figure 3a,b shows the ATR-IR spectra of the SPC before (black line) and after exposure to 10 bar of CO2 followed by ambient conditions for the indicated times. The two regions that appear in the ATR-IR spectra (outlined by the dashed-line boxes) after the CO2 sorption are of interest. The first IR peak, located at 2,345 cm⁻¹, is assigned to the anti-symmetric CO2 stretch, confirming that CO2 was physisorbed and evolving from the SPC sorbent. The other IR band, centred at 1,730 cm⁻¹, is attributed to the C=O symmetric stretch from the poly(CO2) on the SPC. Interestingly, this carbonyl peak is only observed with the porous heteroatom-doped carbon, such as the SPC and NPC. Other porous sorbents without nucleophilic species, such as ZIF-8 and activated carbon, only showed the physisorbed or evolving CO2 peak (~2,345 cm⁻¹) (Supplementary Figs 4 and 5). Once the CO2-filled SPC returned to ambient pressure, the key IR peaks attenuated over time and disappeared after 20 min. Based on this data, the ATR-IR study confirmed the poly(CO2) formation. Raman spectroscopy was further used to probe individual chemical bond vibrations as shown in Fig. 3c. The carbonaceous graphitic G-band and defect-derived diamondoid D-band were at 1,590 and 1,350 cm⁻¹ (refs 19,20). The peak at 798 cm⁻¹ can be attributed to the symmetric stretch of the C–O–C bonds21,22, which was not observed for the other nucleophile-free porous materials, suggesting that the poly(CO2), with the (~O–C(=O)O)n⁻ moiety, was formed. The monoanionic carbonate and carbamate anions within the channels of the SPC and NPC, respectively, were the likely initiation points for the CO2 polymerization since no poly(CO2) was seen in activated carbon (Supplementary Fig. 5). Furthermore, ¹³C NMR also confirms the presence of the poly(CO2) formation. The sorbent gives a broad signal characteristic of aromatic carbon (Fig. 3d, bottom). After exposure to CO2, a relatively sharp signal on top of the broad sorbent signal appears at 130.6 p.p.m., which can be assigned to the CO2 that is evolving from the support. A sharp signal also appears at 166.5 p.p.m. (Fig. 3d, middle), which is characteristic of the carbonyl resonance for poly(CO2). Both of these signals are gone 19 h later (Fig. 3d, top), see Supplementary Note 3.

Compared with secondary amine-based CO2 sorbents where maximum capture efficiency is 0.5 mol CO2 per mol N (2 RNH₂ + CO2 → RNH₂+O2CNHR), the SPC and NPC demonstrate a unique mechanism during the CO2 uptake process resulting in their remarkably higher CO2 capacities versus S or N content (8.1 atomic % of S and 6.2 atomic % of N in the SPC and NPC, respectively, by XPS analysis). Figure 3e,f shows a mechanism to illustrate this CO2 fixation by polymerization. Dimeric CO2 uptake has been crystallographically observed in metal complexes22, and polymeric CO2 has been detected previously but only at extremely high pressures of ~15,000 bar (ref. 21). The spectroscopic determination here confirms poly(CO2) formation at much lower pressures than formerly observed.

A series of porous materials with and without the nucleophilic heteroatoms were tested to compare their CO2 capture performance up to 30 bar at 30 °C (Fig. 4a). The SPC had the highest CO2 capacity; the NPC, activated carbon, zeolite 5A and ZIF-8 had lower capacities. Although NPC had significantly lower CO2 capacity than SPC, its uptake performance could be improved by 21 wt% after H2 reduction at 600 °C, producing reduced-NPC (R-NPC) with secondary amine groups (Fig. 1a). Even though the surface area of R-NPC (1,450 m² g⁻¹) is only slightly greater than that of the activated carbon (1,430 m² g⁻¹), the presence of the amine groups induces the formation of the poly(CO2) under pressure, promoting the CO2 sorption efficiency of the R-NPC. The pore volume of R-NPC is 1.43 cm³ g⁻¹.

Purification of natural gas from wells relies upon a highly CO2-selective sorbent, especially in a CH4-rich environment. Thus, CH4 uptake experiments were carried out on three different types of porous materials, SPC, activated carbon and ZIF-8. Figure 4b–d compares CO2 and CH4 sorption over a pressure range from 0 to 30 bar at 23 °C. In contrast to the CO2 sorption, the CH4 isotherms for these three sorbents reached equilibrium while the system pressure was approaching 30 bar. The order of the CH4 uptake capacities was correlated to the surface area of the sorbents. Comparing these sorbents, the observed molecular ratio of sorbed CO2 to CH4 (nCO2/nCH4) for the SPC (2.6) was greater.

**Figure 2 | CO2 uptake measurements.** (a) Volumetric and gravimetric uptake of CO2 on SPC at different temperatures and pressures. Those designated with “*” were recorded volumetrically at Rice University. That designated with ‘+’ was performed volumetrically at NIST. That designated ‘w’ was measured gravimetrically at NIST. All gravimetric measurements were corrected for buoyancy. (b–d) Three consecutive CO2 sorption-desorption cycles on the SPC over a pressure range from 0 to 30 bar at 30 °C. All solid circles indicate CO2 sorption, while the open circles designate the desorption process. (e) Volumetric SPC CO2 sorption isotherms at 23 °C and 50 °C over a pressure range from 0 to 1 bar.
than that for the activated carbon (1.5) and ZIF-8 (1.9). In addition, the density of the SPC calculated using volumetric analysis is sixfold higher than in the ZIF-8 (2.21 versus 0.35 g cm\(^{-3}\)) and threefold higher than the zeolite 5A (2.21 versus 0.67 g cm\(^{-3}\)). The high CO\(_2\) capacity and high density observed for SPC greatly increase the volume efficiency, which would reduce the volume of the sorption material for a given CO\(_2\) uptake production rate.

Figure 3 | Spectral changes before and after sorption-desorption and polymerization mechanism. (a, b) ATR-IR, (c) Raman and (d) 50.3 MHz \(^{13}\)C MAS NMR spectra before and after CO\(_2\) sorption at 10 bar and room temperature. All spectra were recorded at the elapsed times indicated on the graphs after the SPC sorbent was returned to ambient pressure. In the NMR experiments, the rotor containing the SPC was tightly capped during the analyses. For the 19 h NMR experiment the same material was left under ambient conditions for 19 h before being repacked in the rotor to obtain the final spectrum. Each NMR spectrum took 80 min to record. (e, f) A mechanism that illustrates the poly(CO\(_2\)) formation in SPC or NPC, respectively, in a higher pressure CO\(_2\) environment. With the assistance of the nucleophile, such as S or N, the CO\(_2\) polymerization reaction is initiated under pressure, and the polymer is further likely stabilized by the van der Waals interactions with the carbon surfaces in the pores.

Figure 4 | Volumetric gas uptake data. (a) Volumetric CO\(_2\) uptake performance at 30 °C of SPC, NPC, R-NPC and traditional sorbents: activated carbon, ZIF-8, and zeolite 5A. Al foil was used as a reference to ensure no CO\(_2\) condensation was occurring in the system at this temperature and pressure. Volumetric CO\(_2\) and CH\(_4\) uptake tests at 23 °C on (b) SPC, (c) activated carbon and (d) ZIF-8 sorbents.
In order to mimic a gas well environment and further characterize the SPC’s selectivity to CO₂, a premixed gas (85 mol% CH₄, 10 mol% CO₂, 3 mol% C₂H₆ and 2 mol% C₃H₈) was used with quadrupole mass spectrometry (MS) detection. The MS inlet was connected to the gas uptake system so that it could monitor the gas effluent from the SPC throughout the sorption–desorption experiment. Supplementary Fig. 6 shows the mass spectrum recorded during the sorption process. The peaks at 15 and 16 amu correspond to fragment and molecular ions from CH₄, while the peaks at 28 and 44 amu are from CO₂ in the premixed gas. Other minor peaks can be assigned to fragment ions from C₂H₆ and C₃H₈. Although the peak at 44 amu can also come from C₃H₈ ions, the contribution is negligible because of the lower C₃H₈ concentration in the mixed gas, and it is distinguishable by the fragmentation ratios in the MS (C₂H₆: m/z = 29 (100), 44 (30); CO₂: m/z = 44(100), 28(11)). The observed intensity ratio of two peaks at 16 and 44 amu (I₁₆/I₄₄ = 9.1) indicates the abundance of CH₄ versus CO₂ in the premixed gas. Once the sorption reached equilibrium under 30 bar, the desorption process was induced by slowly venting into the MS system. The I₁₆/I₄₄ ratio reduced to 0.7. The SPC has been shown to have 2.6-fold higher CO₂ than CH₄ affinity at 30 bar when using pure CO₂ and CH₄ as feed gases (Fig. 4b). If the binding energy of CH₄ and CO₂ are assumed to be similar, and the partial pressure of CH₄ versus CO₂ in the premixed gas is considered (P(CH₄)/P(CO₂) = 8.5), then the number of sorbed CH₄ should be ~3.3-times more than that of the sorbed CO₂. Typically, CO₂-selective materials have selective sites and once the CO₂ occupies those sites, the selectivity significantly decreases and the materials behave as a physiosorbert with lower selectivities at higher pressures. On the contrary, here the SPC demonstrates much higher CO₂ selectivity than expected since the chemisorbed sulphur-initiated poly(CO₂) chain displaces physiosorbed gas.

Under the mechanism described here for CO₂ polymerization in the channels of inexpensive nucleophilic porous carbons, these new materials have continuous selectivity toward CO₂, limited only by the available pore space and pressure. Through development of these enhanced stationary phase sorbents, capture and reinjection of CO₂ at the natural gas sites could be realized, thereby leading to greatly reduced CO₂ emissions from natural gas streams. CO₂ fixation through polymerization is disclosed here as a major advance for future capture and possibly storage of this greenhouse gas.

**Methods**

**Instrumentation at Rice University.** An automated Sieverts instrument (Setaram PCTPro) was adopted to measure gas (CO₂, CH₄ or premixed gas) sorption properties of materials. Typically, ~70 mg of sorbent was packed into a ~1.3 ml of stainless steel sample cell. The sample was pretreated under vacuum (~3 mm Hg) at 130 °C for 6 h and the sample volume was further determined by helium before the uptake experiment. At each step of the measurement, testing gas was expanded from the reference reservoir into the sample cell until the system pressure reached equilibrium. A quadrupole mass spectrometer (Setaram RGA200) was connected to the Sieverts instrument so that it could monitor the gas effluent from the sorbent throughout the entire sorption–desorption experiment. With the assistance of a hybrid turbomolecular drag pump, the background pressure of the MS can be controlled lower than 5 × 10⁻⁸ Torr. All material densities were determined using volumetric analysis on this same instrument.

XPS was performed using a PHI Quanta XSM Scanning X-ray Microprobe with a base pressure of 5 × 10⁻⁸ Torr. Survey spectra were recorded in 0.5 eV step size and a pass energy of 140 eV. Elemental spectra were recorded in 0.1 eV step size and a pass energy of 26 eV. All spectra were standardized using C1s peak (284.5 eV) as a reference.

The ATR-IR experiment was conducted using a Fourier transform infrared spectrometer (Nicolet Nexus 670) equipped with an attenuated total reflectance system (Nicolet, Smart Golden Gate) and a MCT-A detector. Raman spectra were measured using a Renishaw inVia Raman Microscope with a 514 nm excitation argon laser.

Scanning electron microscope images were taken at 15 KeV using a JEO-L6500 F field emission microscope. High-resolution TEM images were obtained with a JEM 2100 F field emission gun TEM.

An automated BET surface analyser (Quantachrome Autosorb-3b) was used for measurements of sorbents’ surface areas and pore volumes based on N₂ adsorption–desorption. Typically, a ~100 mg of sample was loaded into a quartz tube that was pretreated at 130 °C under vacuum (~5 mm Hg) in order to remove sorbates before the measurement. MAS NMR spectra were recorded on a Bruker Avance III 4.7 T spectrometer with a standard MAS probe for 4 mm outer diameter rotors.

**Instrumentation at NIST.** Volumetric CO₂ sorption measurements were carried out on computer-controlled custom-built volumetric sorption equipment previously described in detail24, with an estimated reproducibility within 0.5% and the standard data error bar of less than 2% compared with other commercial instruments. An amount of ~79 mg of sample was used for the experiments. Sample degassing, before the CO₂ sorption experiment, was done at 130 °C under vacuum for 12 h.

Gravimetric CO₂ sorption measurements were performed on a high pressure thermal gravimetric equipment (Model: TGA HP90) from TA Instruments. An amount of ~15 mg of sample was used for the experiment. Sample degassing, before CO₂ sorption experiment, was done at 130 °C under vacuum for 12 h.

**Synthesis of SPC.** Poly[(2-hydroxymethyl)thiophene] (PTh) (Sigma–Aldrich) was prepared with FeCl₃ (ref. 24) In a typical synthesis, 2-thiophenemethanol (1.5 g, 13.1 mmol) in CH₃CN (10 ml) was slowly added under vigorous stirring to a slurry of FeCl₃ (14.5 g, 89.4 mmol) in CH₃CN (50 ml). The mixture was stirred at room temperature for 24 h. The polymer (PTh) was separated by filtration over a sintered glass funnel, washed with distilled water (~1 l) and then with acetone (~200 ml). The polymer was dried at 100 °C for 12 h to afford 1.21 g (96% yield) of the desired compound.

The PTh was activated by grinding PTh (500 mg) with KOH (1 g, 17.8 mmol) with a mortar and pestle and then heated under Ar at 600 °C in a tube furnace for 1 h. The Ar flow rate was 500 sccm. After cooling, the activated sample was thoroughly washed 3 × with 1.2 M HCl (1 l) and then with distilled water until the filtrate attained pH 7. The SPC sample was dried in an oven at 100 °C to afford 240 mg of the black solid SPC. The BET surface area and pore volume were 2,500 m² g⁻¹ and 1.01 cm³ g⁻¹, respectively.

**Synthesis of NPC.** Commercial polycarboxylonitrile (PAN, 500 mg, average Mₙ 150,000, Sigma–Aldrich) powder and KOH (1,500 mg, 26.8 mmol) were ground to a homogenous mixture in a mortar. The mixture was subsequently carbonized by heating to 600 °C under Ar (500 sccm) in a tube furnace for 1 h. The Ar flow rate was 500 sccm. After cooling, the activated sample was thoroughly washed 3 × with 1.2 M HCl (1 l) and then with distilled water until the filtrate attained pH 7. Finally, the carbon sample was dried in an oven at 100 °C to afford 340 mg of the solid black NPC.

To produce R-NPC, the activated carbon (270 mg) was further reduced by 10% H₂ (H₂/Ar = 50.450 sccm) at 600 °C for 1 h to provide 255 mg of the final material. The BET surface area and pore volume were 1,450 m² g⁻¹ and 1.43 cm³ g⁻¹, respectively.

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Author contributions

C.-C.H. designed and performed the experiments and wrote the manuscript. J.J.T. conducted some of the experiments. C.K. helped with the uptake analyses at Rice University. L.E. performed the uptake experiments at NIST. L.B.A. performed the solid state NMR and analyses. J.M.T. oversaw all phases of the research, suggested many of the experiments and revised the manuscript. All authors discussed and commented on the manuscript.

Additional information

Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing financial interests: Rice University has filed patent applications (PCT/US2013/021239, 61/839,567, 61/865,296, 61/486,323) on the carbon stationary phases and the mechanisms of fixation described here for CO2 capture from natural gas. Apache Corp. has licensed the intellectual property (agreement no. 0112011). None of the authors own rights to the technology described here and none hold stock in Apache Corp., aside from what might be held in broad mutual funds.

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In this Article, we reported the synthesis of nucleophilic sulfur- and nitrogen-containing porous carbons and their carbon dioxide uptake performance. Specifically, we described a mechanism where the carbon dioxide polymerized in the channels of the porous support. Since the publication of the Article we have been unable to reproduce the infrared, Raman and solid-state $^{13}$C-NMR spectra that supported this mechanism; these data had been generated in the laboratory of J.M.T. During our efforts to reproduce the infrared spectra, the band centred at 1,735 cm$^{-1}$ was not as pronounced as in the published data. The Raman band at 798 cm$^{-1}$ was observed on the occasion but disappeared with further focusing of the instrument; and the 166.5 p.p.m. peak in the solid-state $^{13}$C-NMR could not be acquired again. While the gas adsorption data are without question and reproduced across laboratories, we are no longer confident in the spectroscopic data supporting the proposed carbon dioxide polymerization mechanism and we, the authors, therefore wish to retract this Article.

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