Supporting Information

Water-Stable Direct Air Capture of CO_2 with Microcapsules of Task-Specific Ionic Liquid and their Electrothermal Regeneration

Luma Al-Mahbobi,[a] Smita S. Dasari,[b] Aidan Klemm,[c] Harry M. Meyer III,[d] Yue Yuan,[d] Micah J. Green,[a,b] Emily Pentzer,[a,e*] Michelle K. Kidder[c*]

a. Department of Materials Science and Engineering, Texas A&M University, College Station, Texas 77843, USA
b. Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843, USA
c. Energy Science and Technology Directorate, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States
d. Physical Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States
e. Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA
*Corresponding Authors: emilypentzer@tamu.edu, kidderm@ornl.gov

Optical Microscopy Images of Capsules

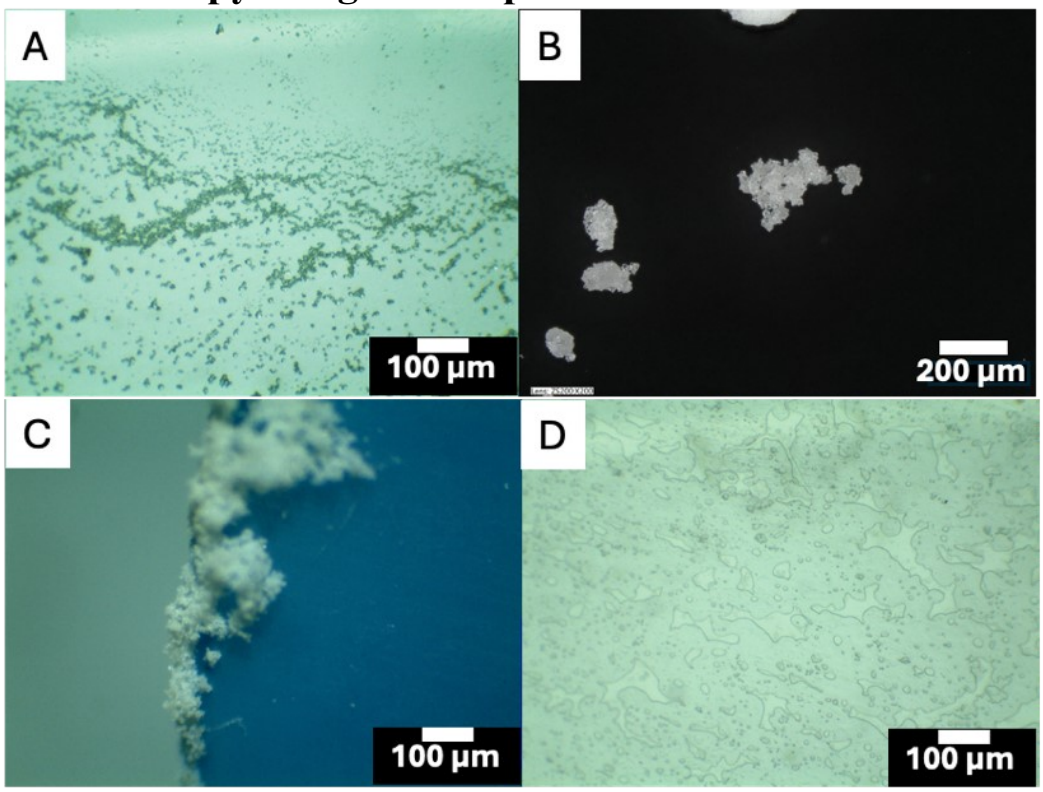

Figure S1. Optical microscopy images of PDMS-PU capsules of [EMIM][2CNpyr] core showing (A) capsules in octane, (B) dry capsules (C) capsules scraped with spatula, and (D) squished capsules.

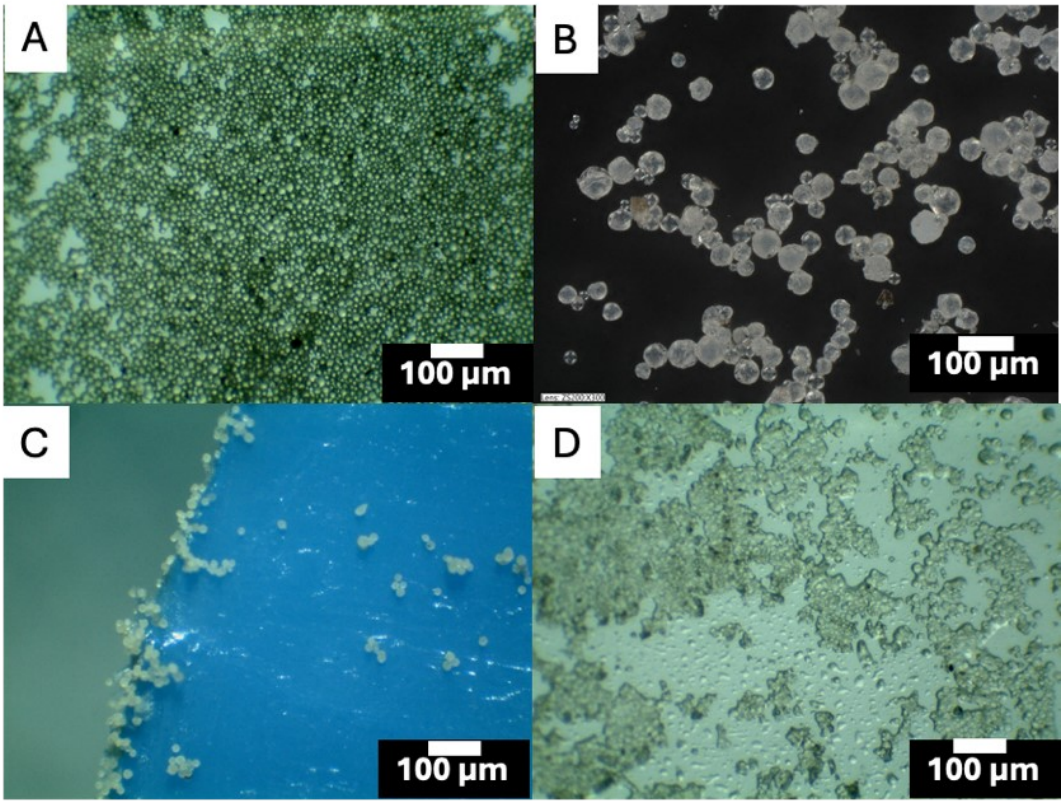

Figure S2. Optical microscopy images of GO-PDMS capsules of [EMIM][2CNpyr] core showing (A) capsules in octane, (B) dry capsules (C) capsules scraped with spatula, and (D) squished capsules.

MGO Characterization

Figure S3 presents the FTIR spectra of M-GO, confirming the functionalization of GO. The characteristic sp^3 C-H stretching vibrations between 2850 and 2950 cm^{-1} indicate the presence of alkyl chains, supporting the alkylation of GO. Additionally, successful PDMS grafting is evident from the Si-C-H (1256 cm^{-1}) and Si-O (1009 cm^{-1}) peaks. The inset image shows MGO (C18-PDMS-GO) dispersed in octane (10 mg/mL), demonstrating its dispersibility in nonpolar solvents, further validating the functionalization.

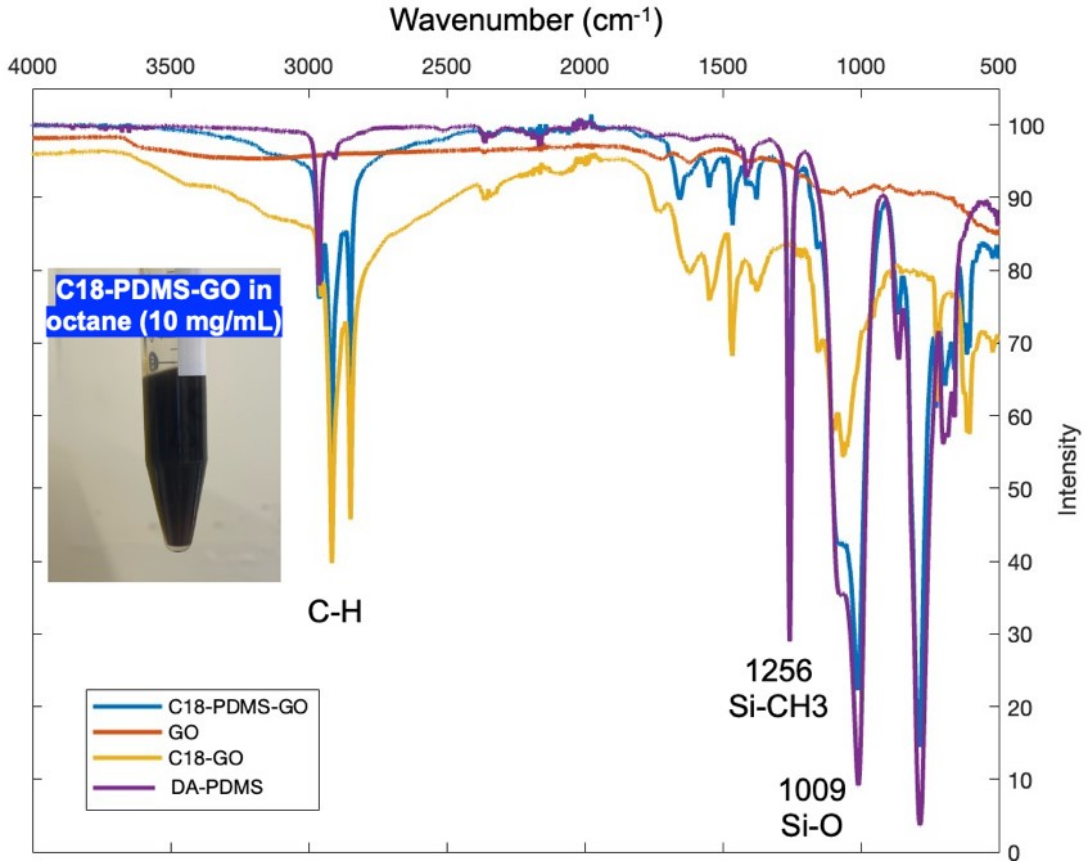

Figure S3. FTIR spectra of GO, C_{18}-GO, MGO (C_{18}-PDMS-GO), and DA-PDMS (diamino-PDMS)

XPS Spectra

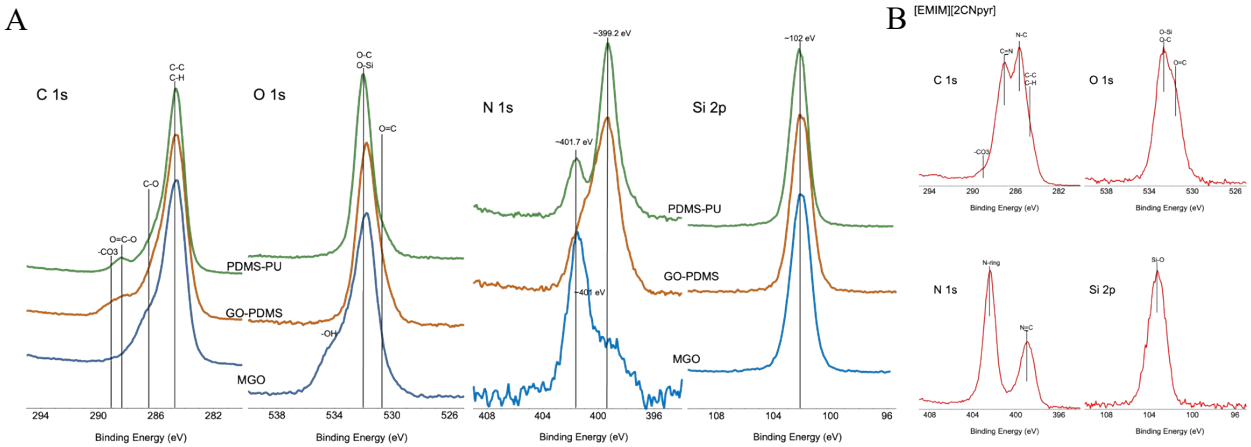

Figure S4. XPS spectra of (A) PDMS-PU, GO-PDMS, MGO (C_{18}-PDMS-GO), and (B) [EMIM][2CNpyr] (The observation of Si 2p binding energy in [EMIM][2CNpyr] may be due to cross-contamination during sample preparation)

Table S1. XPS at.% surface composition

	Surface Composition (at.%)						
	C	**N**	**O**	**Si**	**S**	**K**	**Mn**
GO	56.0	4.1	34.4	0.7	3.8	0.5	0.5
C_{18}-PDMS-GO	57.8	2.7	23.0	15.8	0.8	0.0	0.0
[EMIM][2CNpyr]	69.3	17.7	9.6	3.3	0.0	0.0	0.0
GO-PDMS	61.0	11.0	17.4	10.7	0.0	0.0	0.0
PDMS-PU	57.1	7.8	19.5	15.6	0.0	0.0	0.0

^{1}H NMR Spectra

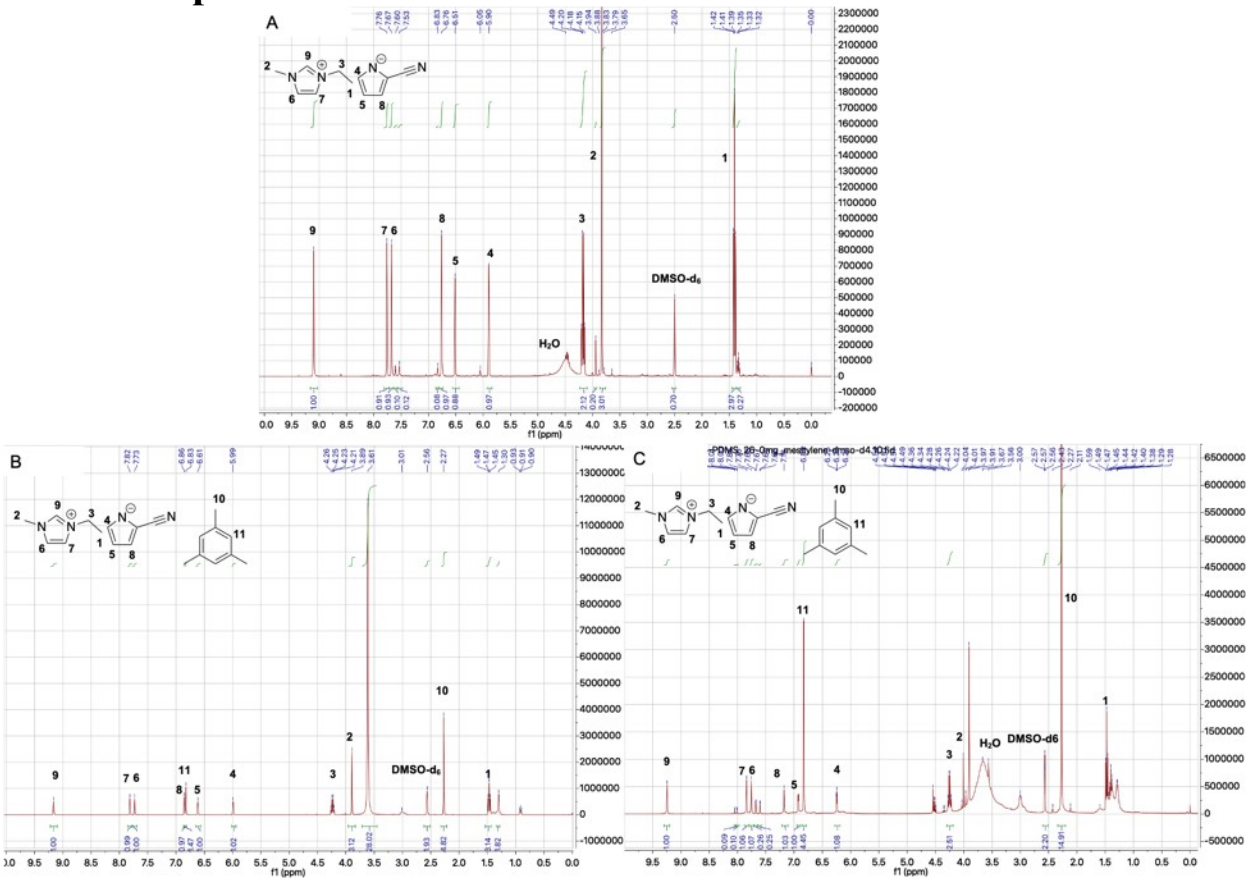

Figure S5. ^{1}H NMR spectra of [EMIM][2CNpyr] in DMSO-d_6 (A) in pure liquid form, (B) extracted from PDMS-PU capsules, and (C) extracted from GO-PDMS capsules with mesitylene used as an internal standard for both capsule types.

Weight% Analysis

Table S2. Core wt% calculations using ^{1}H NMR raw data analysis following the same procedure previously reported by Pentzer et al.[1]

Scheme	Extracting TSIL from capsules: ^{1}H NMR analysis		
Preparation method	PDMS-PU (or GO) capsules were weighed to ~20 mg and dispersed in 1 mL of 0.039M mesitylene in DMSO-d_6 solution. The dispersion was sonicated for 60 min to extract the liquid core. The TSIL solution was collected by syringe filtration and transferred to an NMR tube.		
Name of capsule sample	PDMS-PU	GO-PDMS	
Weight of sample used (mg)	23.1	26.0	
Mesitylene content present in the sample	0.039 mmol		
Relative integration of the 4 hydrogens on the sp2 carbons of TSIL (labeled 5, 6, 7, & 8 in **Figure S4**) to the 3 hydrogens on the benzyl ring of mesitylene at 6.8 ppm	1.49	0.70	
Weight of [EMIM][2CNpyr] (mg)	11.8	5.5	
Average wt% [EMIM][2CNpyr]	58.7	20	
Preparation method (for GO-PDMS)	Gravimetrically by weighing the capsules and shells before and after grinding and washing the liquid core out		
Sample #	Weight before extraction (mg)	Weight after extraction (mg)	Wt%
1	14.95	8.66	57.9
2	15.11	7.80	51.6
3	15.25	7.74	50.8
4	15.34	7.74	50.5
Average wt%	52.7		

CO_2 Capture Performance

To understand how much these shell materials contribute to CO_2 uptake, hollow shells were created. This involved using a non-reactive IL, [BMIM][BF_4], to form capsules, then extracting it to leave behind empty shells with the same PDMS-PU and GO-PDMS composition. It is important to note, however, that when using the TSIL, the shell composition slightly changes. During synthesis, the TSIL chemically interacts with the shell components, evident in the XPS data. Additionally, the TSIL tends to plasticize into the shell walls, leading to partial retention even after extraction. Thus, for a more accurate control study, capsules were made with [BMIM][BF_4] and fully extracted to create hollow shells. The DAC capacities of these shells were gravimetrically measured to reach 0.04 and 0.03 mol kg^{-1} for PDMS-PU and GO-PDMS, respectively (**Figure S6B**).

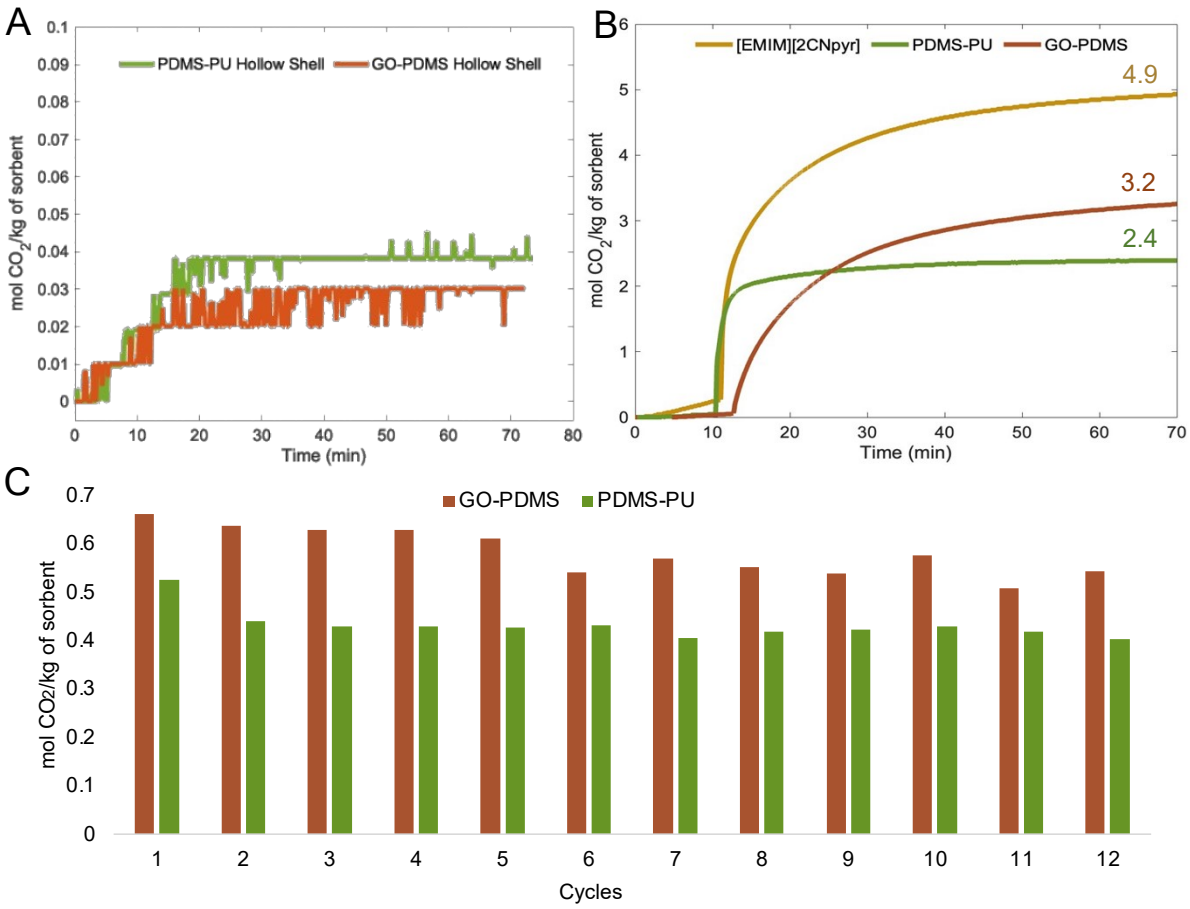

Figure S6. (A) TGA pure CO_2 sorption at 1 bar and 30˚C, and desorption at 65 ˚C under pure N_2 of [EMIM][2CNpyr] bulk, PDMS-PU, and GO-PDMS capsules. TGA 410 ppm CO_2 in N_2 (1 bar, 30 ˚C) (B) of hollow shells, and (C) sorption/desorption cycles of PDMS-PU and GO-PDMS capsules.

RF Heating of PDMS-PU Capsules

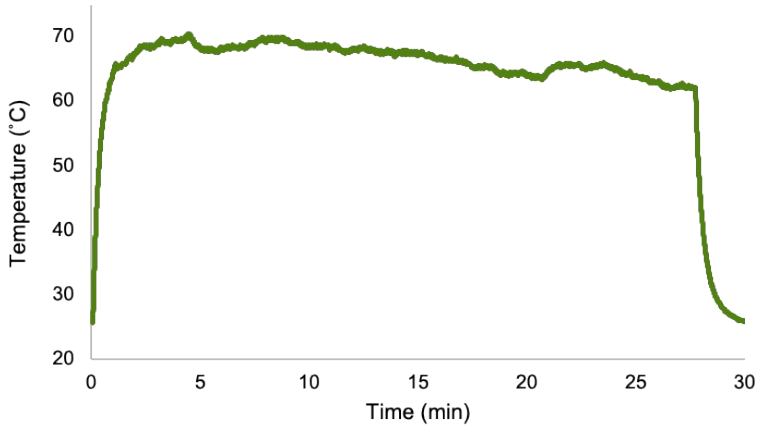

Figure S7. RF heating of PDMS-PU capsules at 1-2W and 123 MHz.

CO_2 Capacity of PDMS-PU Capsules Before and After Soaking in Water

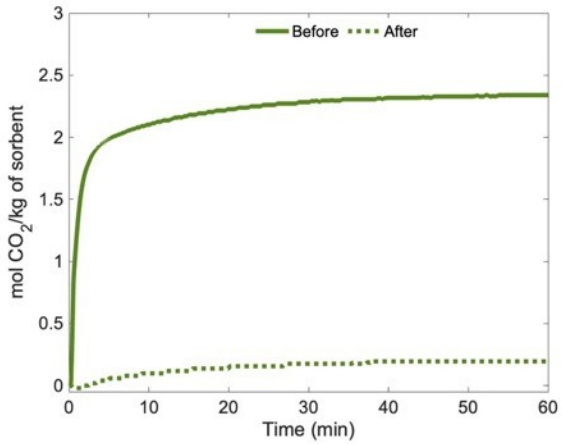

Figure S8. TGA pure CO_2 capacities (1 bar, 30 ˚C) of the PDMS-PU capsules before and after immersion in water for 24 hours.

Optical Microscopy Images of Alternative Core Liquids

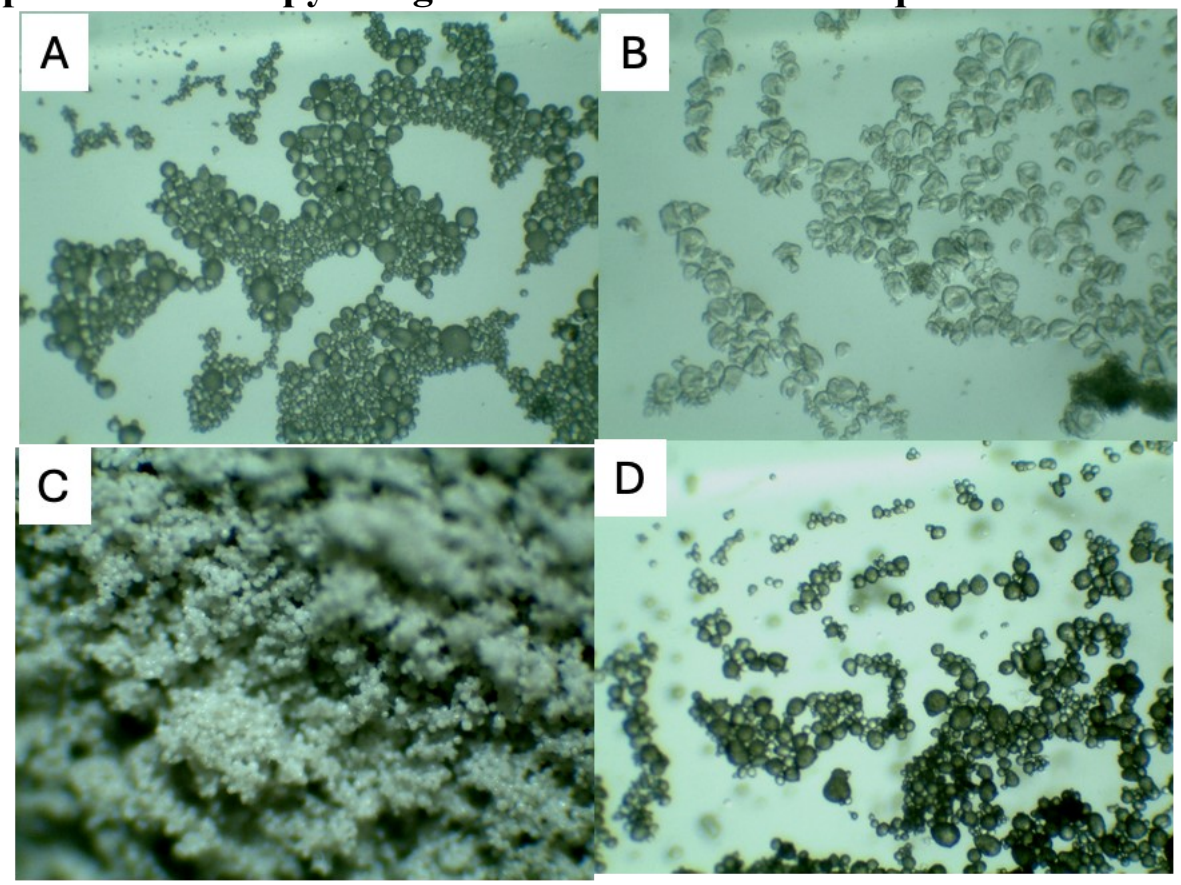

Figure S9. Optical microscopy images of (A,B) PDMS-PU and (C, D) GO-PDMS capsules of (A, C) [BMIM][BF_4] core, and (B,D) PEI core.

References

(1) Gaur, S. S.; Edgehouse, K. J.; Klemm, A.; Wei, P.; Gurkan, B.; Pentzer, E. B. Capsules with Polyurea Shells and Ionic Liquid Cores for CO_2 Capture. *J. Polym. Sci.* **2021**, *59* (23), 2980–2989. https://doi.org/10.1002/pol.20210342.