Supporting Information For

Title

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Table of Contents

I. General Experimental Details

Unless otherwise stated, all starting materials and chemical were obtained from Sigma-Aldritch commercial suppliers without purification. Trifluoro-ethanol (TFE) was obtained from Halogen Inc. Disperbyk-130 was obtained from BKY Additives & Instruments. NaOH was obtained from Fisher Scientific. Sylgard®184 Silicone Elastomer Base and Curing Agent were obtained from Dow Corning.

Images of microvascular units were obtained using a Zeiss Axio Observer.A1 Microscope at 2.5X magnification. Scanning electron microscopy (SEM, FEI Quanta FIB) was used to image microvascular images using low voltage setting (1keV). Microscale x-ray computed tomography (μCT) was performed using a 3D tomographic x-ray transmission microscope (MicroXCT-200) through the UCSF Biomaterials and Bioengineering MicroCT Imaging Facility. Settings of 80keV (8W power), 60mm source to sample distance, 20mm detector to sample distance, 5s exposure time, 753 projects, and 5μ reconstruction voxel size were used. Unit channels were loaded with gallium as a contrast agent. UV-Vis absorption spectra were obtained using a Varian Cary 50 Scan UV-Visible Spectrophotometer. Plastibrand® Disposable Cuvettes with a path length of 1 cm and scanning range from 400 to 900nm was used. Fluid dispensing tips were provided by Nordson EFD.

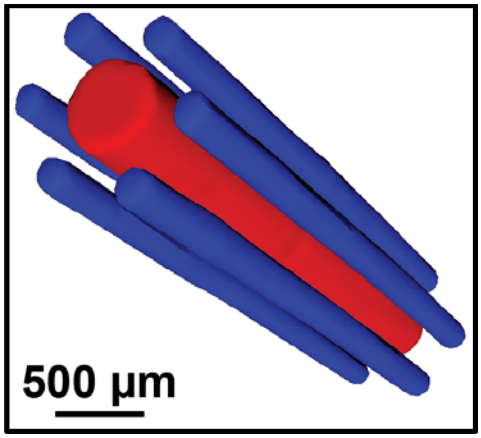

Figure S-1. µCT image of 200/200 3D Hexagonal

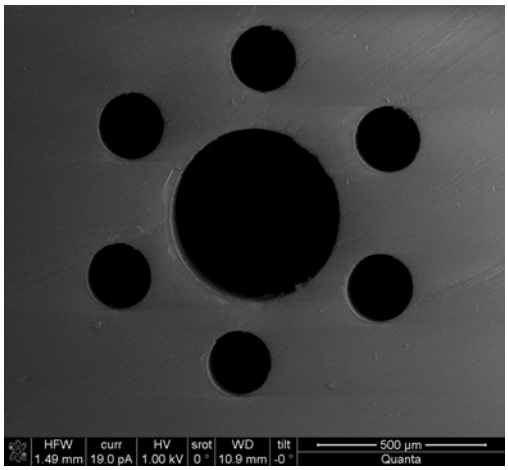

Figure S-2. SEM image of 200/500 3D Hexagonal channels.

II. Test-Sample Fabrication

Fibers were treated according to the Vaporization of Sacrificial Components (VaSC) technique with some modifications.[1] 800 mL of treatment solution was used (400 mL deionized water, 400 mL TFE, 50 g tin oxalate, 20 g disperbyk-130, 0.5 g). Fibers were wound around a custom

spindle and placed in the solution. The solution with fibers was agitated with a digital mixer (IKA RW20) at 250 RPM for 48 h at 25° C.

Figure S-3. Custom spindle for fibers to wrap

Polydimethylsiloxane (PDMS) was created using mixtures of the Slygard 184 silicone elastomer base and curing agent with a 10:1 ratio between base and curing agent inside paper cups. The mixtures were then degassed using a rough vacuum pump and glass bell jar for 15 minutes.

Treated fibers were patterned using laser micromachined brass plates from Laserod. Fibers were strung through matching holes on a pair of plates which were then screwed onto a delrin mold box with dimensions of 25×25×25 mm. Fibers were tensioned until taut on a custom board with three pairs of guitar tuning pegs on either side. Fibers were strung through the holes in the tuning pegs three times to prevent slipping. The degassed PDMS mixtures was poured into the mold and heated at 65°C for 1 h using a Breville Smart Oven to complete the polymerization reaction.

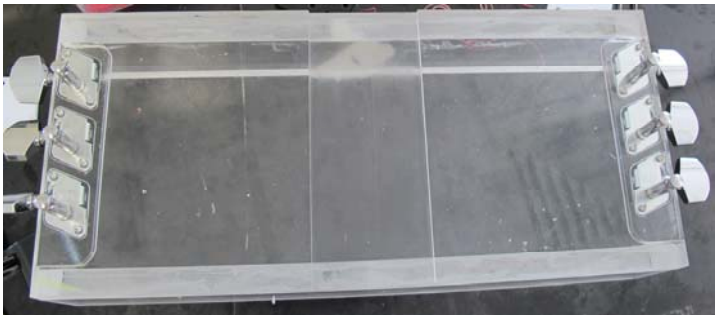

Figure S-4. Custom molding board. Guitar tuners on either side provide tensioning for fibers

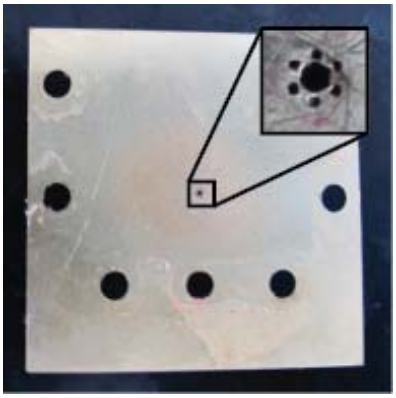

Figure S-5. Laser-etched micromachined brass plates. Fibers are strung through the holes in the end caps, providing the desired pattern.

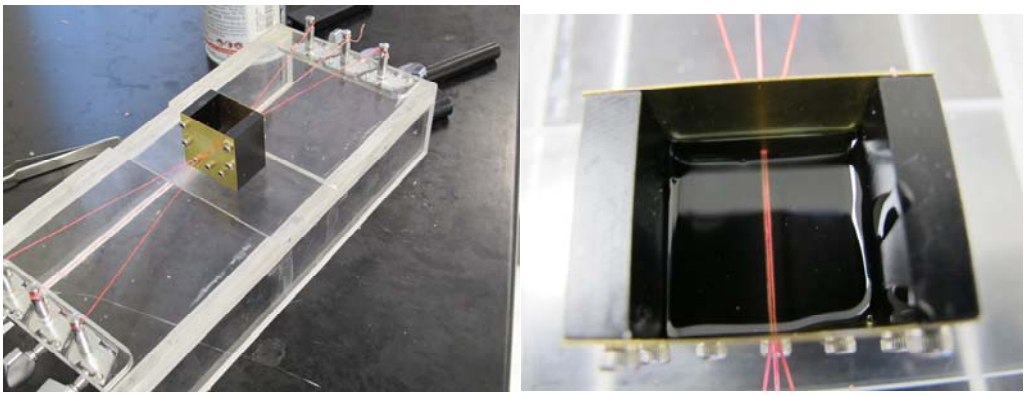

Figure S-6. Assembled molding setup. Fibers are tensioned through the brass end caps using the tuning board. PDMS is poured into the first mold box

The units were then removed from the first mold and placed into a second mold box with dimensions of 25×25×50 mm. The fibers were separated and threaded through PDMS end-caps which were screwed onto the mold box. Syringe needles (B-D PrecisionGlide 18G1 Needle) were inserted through the PDMS end caps and fibers were threaded through the needles. The needles were removed leaving the fibers in the end caps. The end caps were screwed onto the larger mold box and fibers were pulled taut by hand. A second mold of PDMS was then cast again at 65°C for 1 h. Longer samples were created using a 25×25×50 mm box as the first mold and 25×25×75 mm box as the second mold.

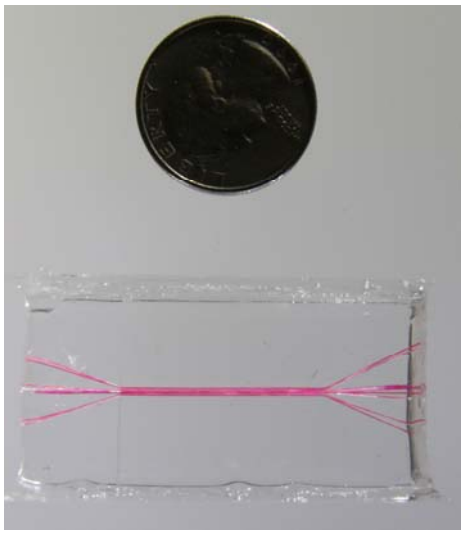

Figure S-7. Test unit after second molding. Fibers are separated into a larger hexagonal pattern for easier loading of channels.

The vascular preforms were removed from the second mold. The remaining fibers extending out of the PDMS were then cut from the edges of the molded shape. The vascular preforms were placed into a sealed vacuum oven (JEIO Tech Vacuum Oven Model OV-11/12) and subjected to a vacuum of 10 torr and heated to 210 °C for 48 h.

III. Experiment for Spatiotemporal Saturation Data Details

Monoethanolamine (MEA) solutions were created with a 7:3 w/w ratio of deionized water and MEA. For solutions with dye (Methyl Blue or Phenolphthalein), 0.6 g of dye are added to every 100 mL of solution. MEA containing dissolved dye was then loaded onto the flanking channels of the test-sample units using precision dispensing tips (Nordson EFD, 32 gauge for 200 μm channels and 25 gauge for 500 μm) and 1 mL syringes (Henke-Sass Wolf 1X100 Norm-Ject). For three-dimensional samples, the top and bottom channel pairs were loaded with MEA containing no. Gas (Airgas, 100% CO_2 or 10% CO_2 balanced with N_2) was then flowed through the central channel at 0.1 L/min controlled via an acrylic flowmeter (VWR, 2" Scale, Range .04-.5 LPM Air). Time-lapsed microscope images were captured with intervals of 4 s at 2.5 magnification focused on the middle of each exchange unit. For mosaic tiled images, 1×6 images were taken with intervals of 12 s were used. Exposure time and white balance were automated by the Zeiss Axiovision software.

For runs with 100% CO2, single, rather than tiled, images of the middle (lengthwise) of exchange units were used due to the faster rate of saturation. 10% CO2 runs used fully tiled images of the entire unit length. Each image measured 5.4 × 4 mm. To analyze the images, rectangular regions of interest utilizing the software were created on the flanking channel. Mean values of the RGB colors within the regions of interest were automatically found for each time-lapsed frame. For methyl blue filled channels, as the CO_2 reacted with the MEA, the color on the flanking channels shifted from clear to blue, the mean red and green values in the selected region of interest in the microscope images decreased. The red values were normalized and set as the scale from 0 to 100 % absorption resulting in the saturation data. For phenolphthalein, the red

values were also used as the reaction between CO_2 and MEA shifted the color of the flanking channels from red to clear.

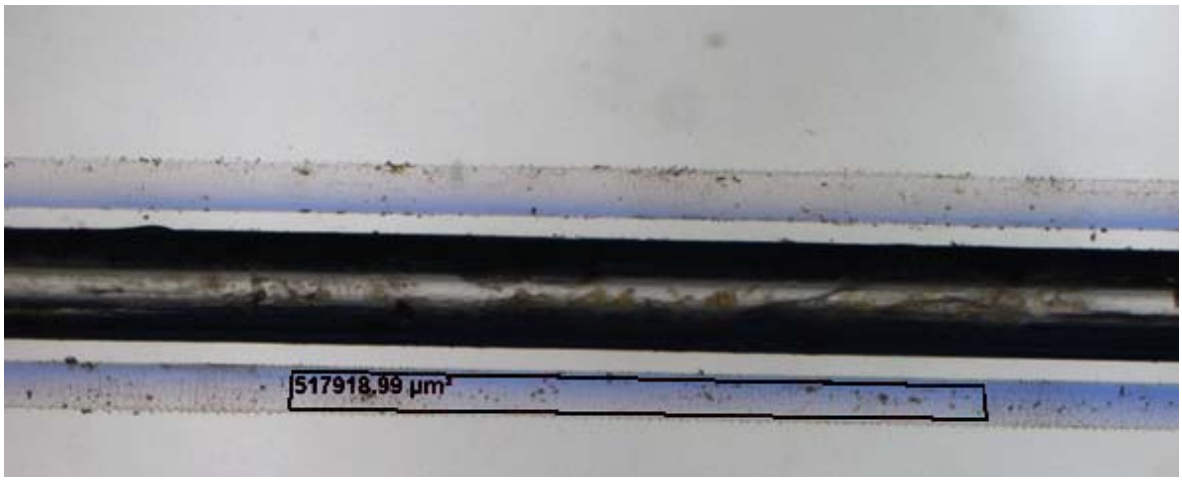

Figure S-8. Example of a region of interest made to gather color data in a channel.

IV. UV-Vis Experimental Details

Solutions of MEA with dye and MEA without dye were mixed in a 1:9 v/v ratio to dilute the color shift. Scintillation vials were filled with 10 mL of the diluted solution and their masses were weighed using an analytic balance (Denver Instruments SI-234). 100% CO_2 was then bubbled into the solutions using plastic tubing at a rate of 0.4 L/min for times ranging from 0 to 10 minutes. The solutions were then weighed again to determine the change in mass and % weight of CO_2 absorbed by the solutions.

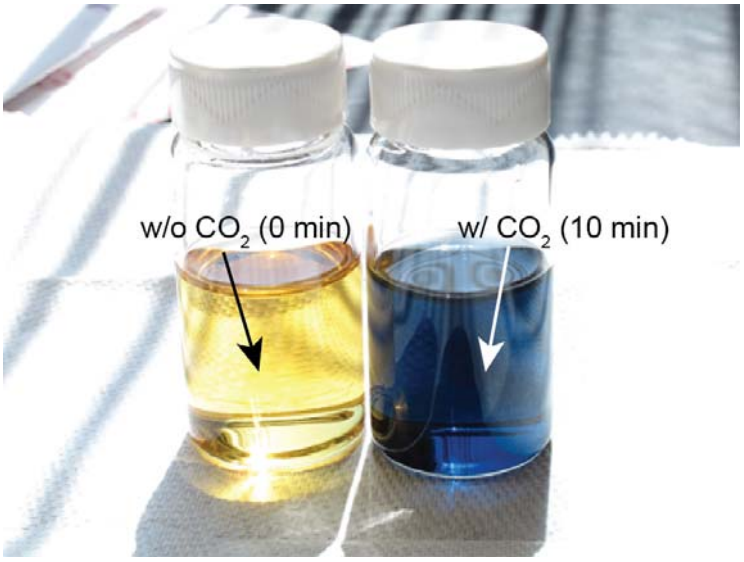

Figure S-9. Scintillation vials containing MEA dyed with methyl blue. On the left is a vial with no CO_2 and on the right is one bubbled with CO_2 for 10 minutes.

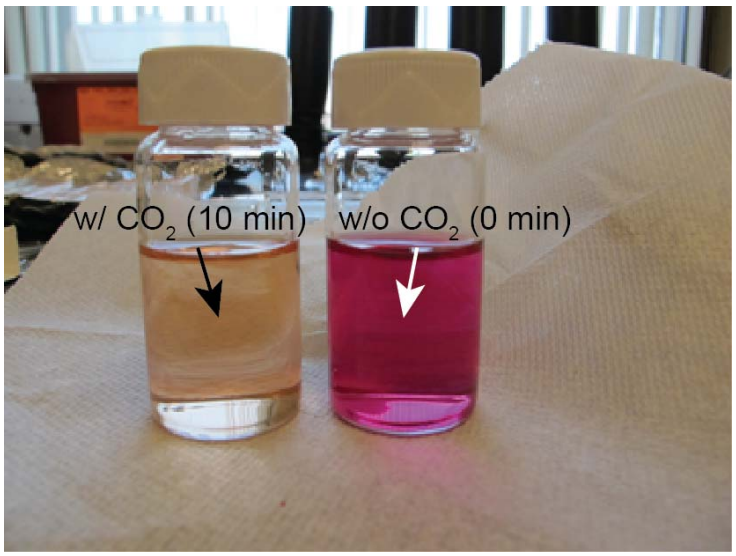

Figure S-10. Scintillation vials containing MEA dyed with phenolphthalein. On the right is a vial with no CO_2 and on the left is one bubbled with CO_2 for 10 minutes.

UV-Vis testing was performed using a Varian Cary 50 Scan UV-Visible Spectrophotometer. A baseline scan was performed before the measurement sets with nothing in the spectrophotometer. Disposable cuvettes were then filled up to ~2 cm in height and scans running from 400 to 900 nm were made using a medium scan rate.

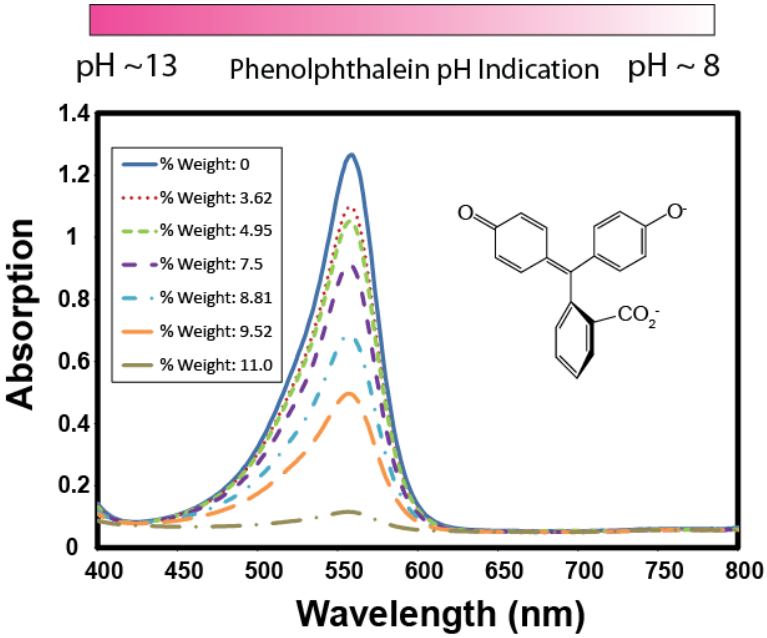

Figure S-11. UV-Vis data for phenolphthalein. Decrease in absorption in the 550 nm range

V. COMSOL Model Construction

To create the simulation model of the units, the COMSOL Multiphysics program was used. Cylinders matching the diameters and patterning were created, with lengths of 8 mm. A surrounding box with dimensions of 4×4×8 mm was created to model the PDMS. Meshes composed of tetrahedrals are created from the geometries to approximate the calculations using finite element solving methods. For the mesh creation, element sizes were calibrated for fluid dynamics beginning with a course mesh. Depending on the geometries, minimum element sizes

would be decreased while maximum element sizes were increased in order to compute the models.

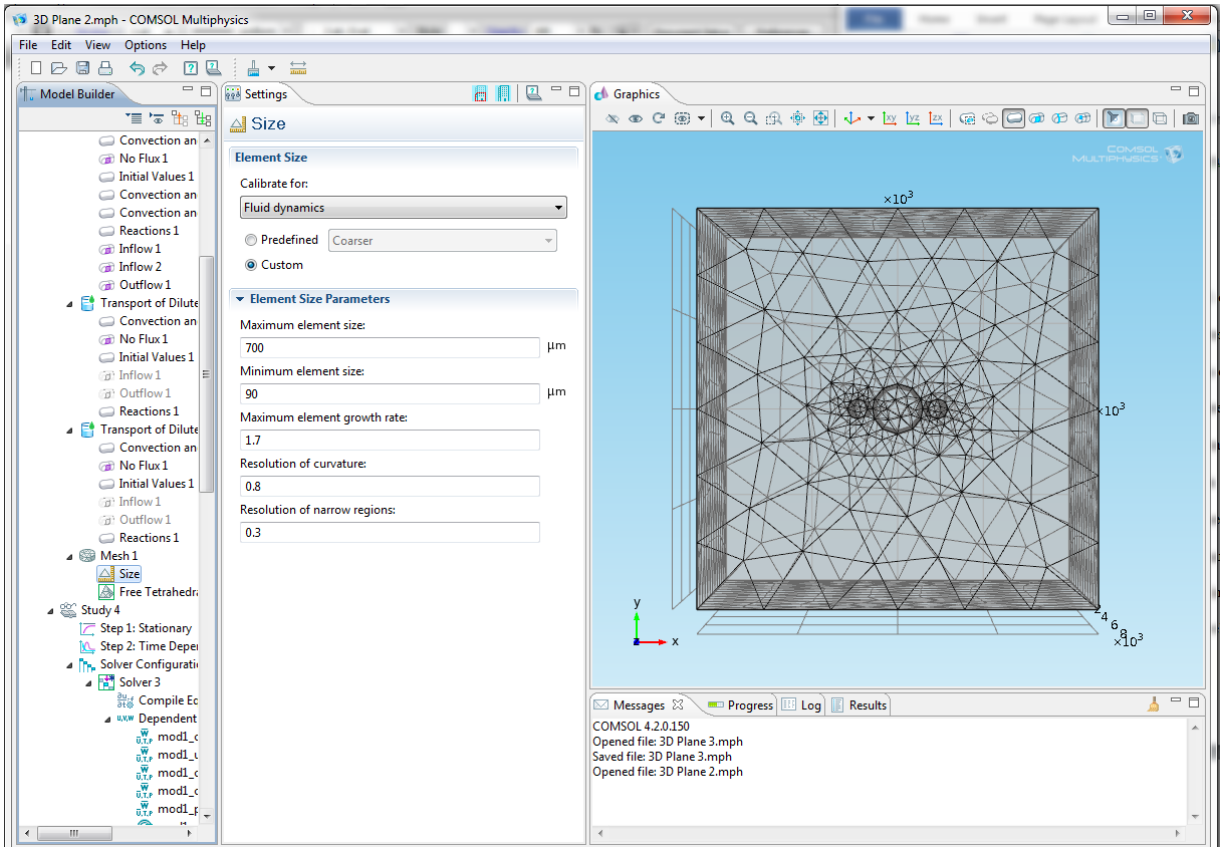

Figure S-12. COMSOL program window. Shown is a 200/500 2D sample with 50µm separation with its mesh constructed.

For the central and flanking channels, the material was defined as carbon dioxide and water respectively, using the default material database. Several parameters are used taken from literature (Figure S-13). [2-8]

Physics Module	Location	Parameter	Value
Laminar Flow	Central Channel	Laminar inflow average velocity	0.000185 m/s
		Entrance length	500 μm
	Flanking Channels	Inflow Pressure	0 Pa
Transport of Diluted Species (All)	All	Velocity field	(spf/fp1)
Transport of Diluted Species (CO_2)	Central Channel	Diffusion coefficient	16 mm^2/s
		Inflow	45 mol/m^3 (4500 for 100% CO_2)
	Flanking Channels	Diffusion coefficient	1.51e-9 m^2/s
		Inflow	0 mol/m^3
		Reaction equation	-6.55*[CO_2]*1000
	PDMS	Diffusion coefficient	7.08e-10 m^2/s
Transport of Diluted Species (MEA)	Flanking Channels	Diffusion coefficient	9.32e-10 m^2/s
		Initial concentration	4900 mol/m^3
		Reaction equation	-6.55*2*[CO_2][MEA]
Transport of Diluted Species ($MEA\text{-}COOH^-$)	Flanking Channels	Diffusion coefficient	9.32e-10 m^2/s
		Initial concentration	0 mol/m^3
		Reaction equation	6.55*[CO_2][MEA]

Figure S-13. Parameter values used to construct COMSOL model.

For the solving settings, the laminar flow module was solved as the first step as a stationary solution with the transport of diluted species modules not in use. The second step solved the transport of diffuse materials as a time dependent solution with all modules in use. The time range and steps depended on the system studied and could be varied with negligible effect on the output. The time-dependent solver used default conditions, except for the use of a generalized alpha time stepping method rather than backward differentiation formulas (BFD). BFD methods

are used typically for their stability, but can have damping effects. The generalized alpha method is similar to second-order BFD, but uses an alpha parameter to control the degree of damping of high frequencies.

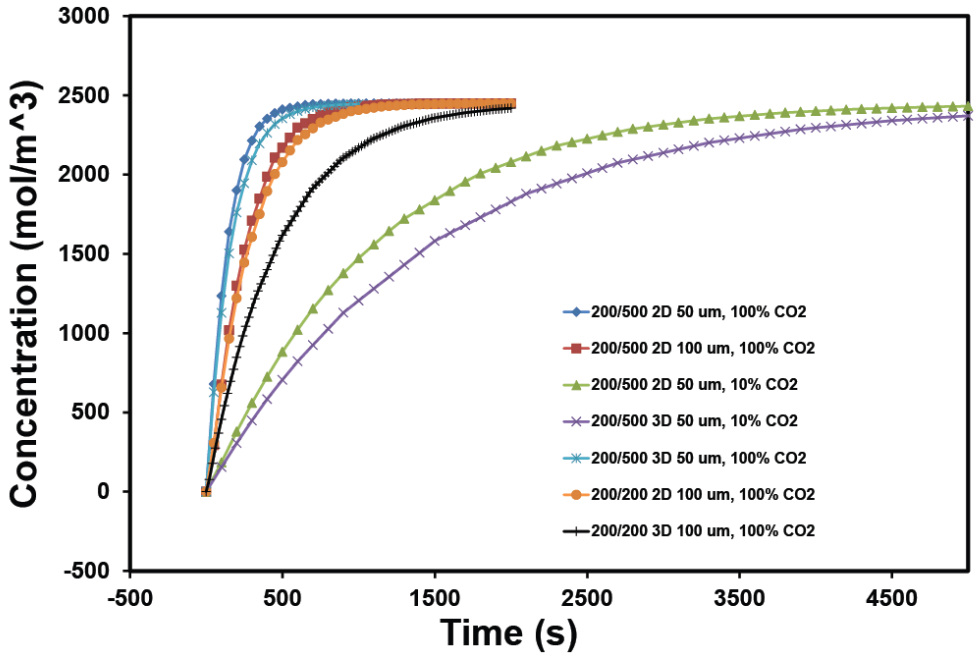

Figure S-14. Summary of various models computed using COMSOL. General trends found experimentally are also present in the model with good agreement.

VI. Specific Surface Area Calculation

To calculate the specific surface area of a unit, the ratio between the surface area of channels containing CO_2 and total unit volume is taken. For a single hexagonal unit, the surface area is taken as the surface area of the central channel, while the volume is taken as the hexagonal perimeter surrounding the entire pattern. The corners of the hexagonal perimeter are approximated as the edges of the outer channels (Figure S-15)

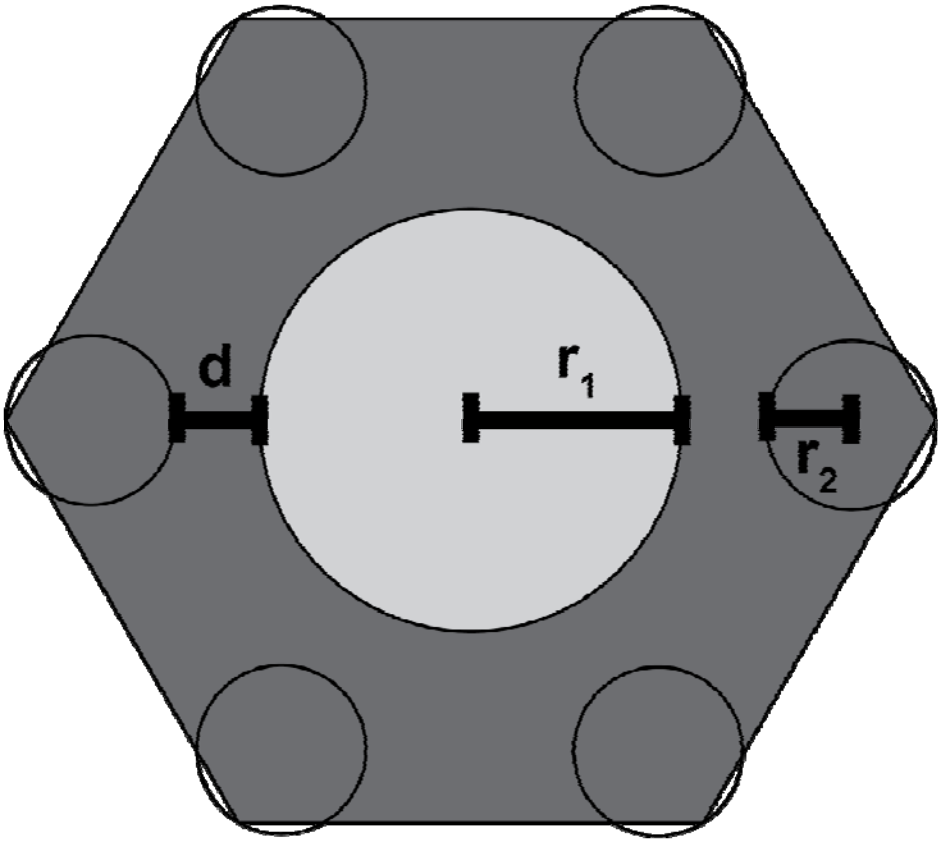

Figure S-15. Geometry used to calculate specific surface area of a 3D gas exchange unit

$$S = \frac{2\pi r_1}{\frac{3\sqrt{3}}{2}(r_1 + d + 2r_2)^2}$$

S = specific surface area (m^2/m^3)

r_1 = CO_2 channel radius (m)

d = channel separation (m)

r_2 =MEA channel radius (m)

To calculate the specific surface area of a larger hierarchy, a similar calculation is carried out for the unit cell of the hierarchy (Figure S-16). By repeating the unit cell, the pattern can be extended indefinitely.

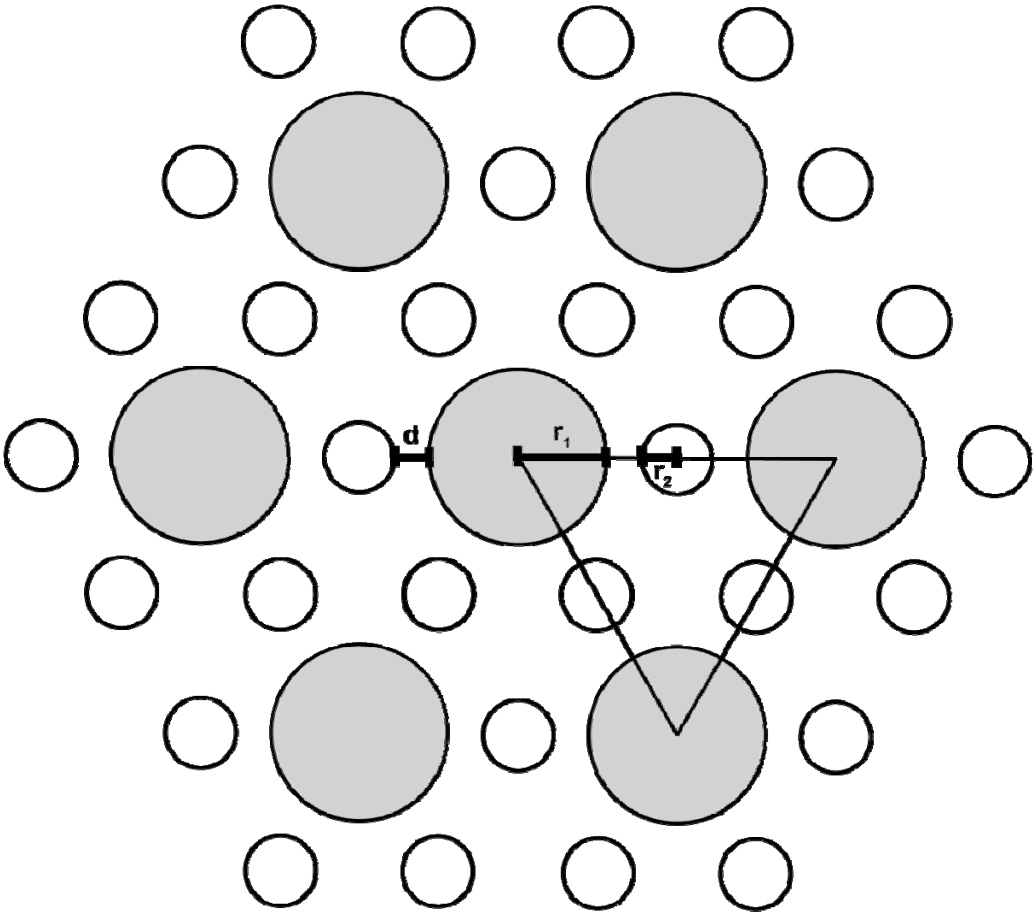

Figure S-16. Geometry used to calculate specific surface area of a larger hierarchy. Shown is a unit cell of 3D pattern.

$$S = \frac{\pi r_1}{\sqrt{3}(r_1 + d + r_2)^2}$$

VII. Mass Transfer Rate Calculation

To compare the difference between 2D and 3D samples, the average mass transfer rate between start time and saturation time was found. Due to the colorimetric method of measurement, which switches from off to on rather than steadily increasing, it was not possible to plot the total amount of CO_2 captured to compare the two geometric arrangements. To calculate the mass transfer rate of the gas exchange units, first the concentration of MEA in a saturated solution is found.

$$c = \frac{1000 * w}{m * (1 - w)}$$

c = saturation concentration (M)

w = saturation weight %

m = molar mass (g/mol)

Assuming a 9.8 wt% as the saturation weight, the saturation concentration becomes 2.47M. Using the time to reach 50% absorption by color as the saturation time, the rate is calculated as follows.

$$R = \frac{1000 * n_1 * \pi {r_1}^2 l * c}{t}$$

R = rate (mol/s)

n_1 = number of MEA channels

r_1 = MEA channel radius (m)

l = channel length (m)

c = saturation concentration (M)

t = saturation time (s)

To finally find the mass transfer, the rate is then divided by the surface area of the channel with flowing CO_2

$$M = \frac{n_{2*}R * 3600}{2\,\pi r_2 l}$$

M = mass transfer rate (mol/m_2•hr)

n_2 = number of CO_2 channels

r_2 = CO_2 channel radius (m)

References

(1) Esser-Kahn, A. P.; Thakre, P. R.; Dong, H.; Patrick, J. F.; Vlasko-Vlasov, V. K.; Sottos, N. R.; Moore, J. S.; White, S. R. *Advanced Materials* **2011**, *23*, 3654-3658.

(2) Webb, K. *Fluid Phase Equilibria* **1999**, *158-160*, 1029-1034.

(3) Merkel, T. C.; Bondar, V. I.; Nagai, K.; Freeman, B. D.; Pinnau, I. *Journal of Polymer Science Part B: Polymer Physics* **2000**, *38*, 415-434.

(4) Versteeg, G. F.; Blauwhoff, P. M. M.; van Swaaij, W. P. M. *Chemical Engineering Science* **1987**, *42*, 1103-1119.

(5) Plaza, J. M.; Wagener, D. V.; Rochelle, G. T. *Energy Procedia* **2009**, *1*, 1171-1178.

(6) Maceiras, R.; Álvarez, E.; Cancela, M. Á. *Chemical Engineering Journal* **2008**, *138*, 295-300.

(7) Haynes, W. *CRC handbook of chemistry and physics : a ready-reference book of chemical and physical data*; 91st ed.; CRC ;;Taylor & Francis [distributor]: Boca Raton Fla. ;London, 2010.

(8) Blauwhoff, P. M. M.; Versteeg, G. F.; Van Swaaij, W. P. M. *Chemical Engineering Science* **1983**, *38*, 1411-1429.