Electronic Supplementary Material (ESI) for Soft Matter.
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Observation of Intensity Dependent Phase-Separation in Photoreactive Monomer-Nanoparticle Formulations under Non-Uniform Visible Light Irradiation

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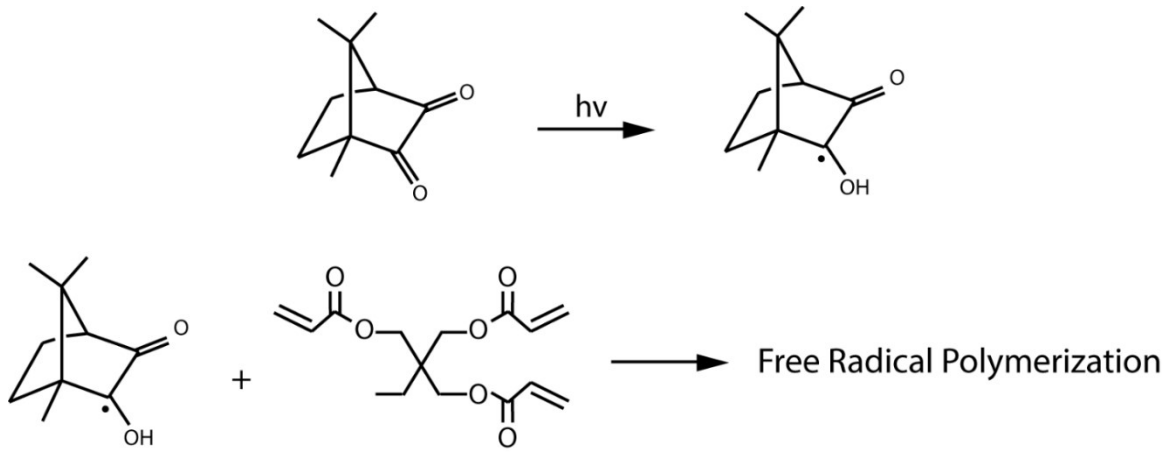


Figure S1: Schematic of the polymerization reaction. The first reaction represents the excitation of a CQ molecule due to absorption of light. This radical then initiates polymerization upon encountering a TMPTA monomer molecule as indicated in step 2

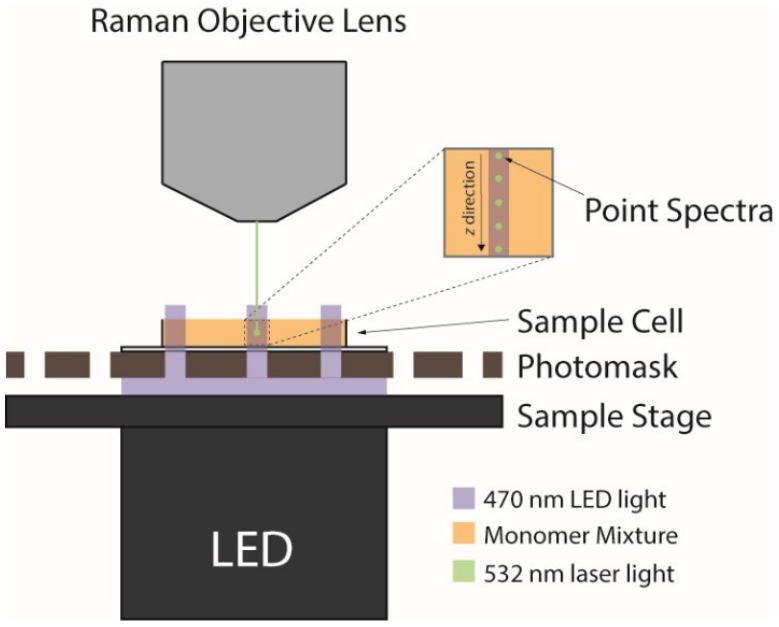


Figure S2: Schematic of the setup used for in-situ Raman spectroscopy measurements. The magnified schematic indicates the z-direction in which individual point spectra were collected over exposure time.

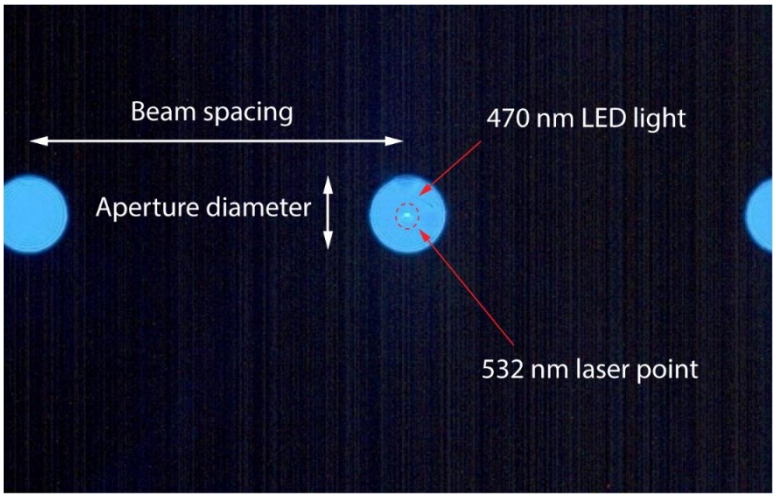


Figure S3: Snapshot of a photomask illuminated with a 470 nm LED indicating beam spacing (200 µm), aperture diameter (40 µm) and position of the 532 nm laser beam used for in-situ Raman spectroscopy measurements. Calculation of laser spot size: λ_{laser} = 532 nm and N_A = 0.4, therefore laser spot size = $\frac{1.22 * \lambda}{N_A}$ = ~1.62 µm.

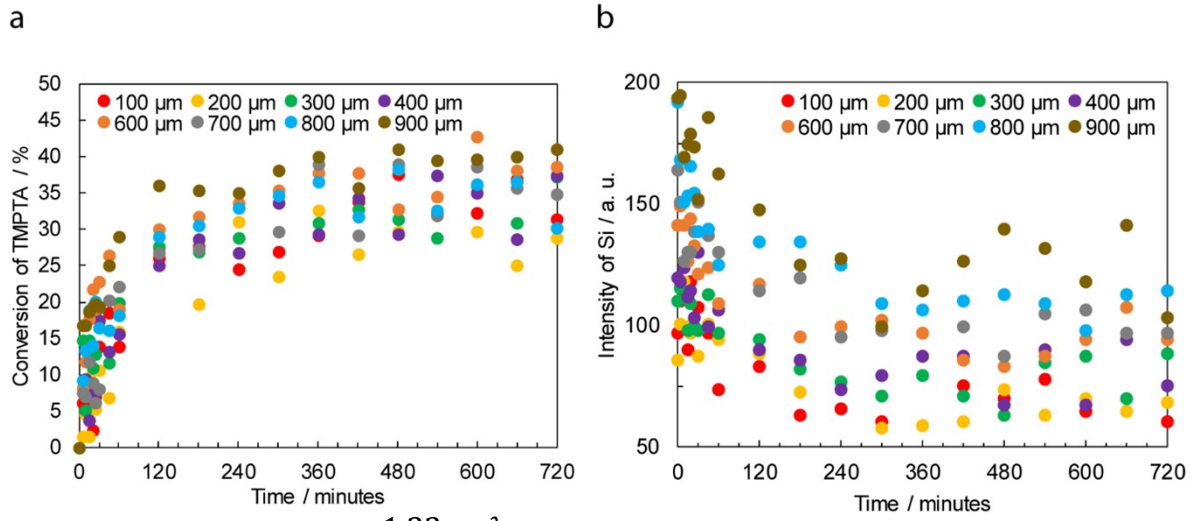


Figure S4: TMPTA conversion and Si intensity profiles over irradiation time at 4 mW/cm^2.

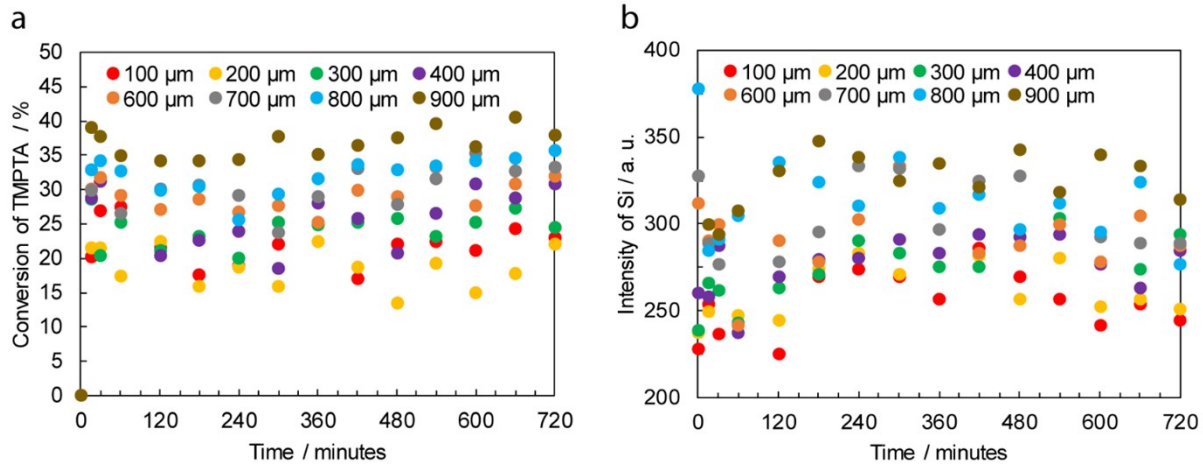


Figure S5: TMPTA conversion and Si intensity profile over irradiation time at 20 mW/cm^2.

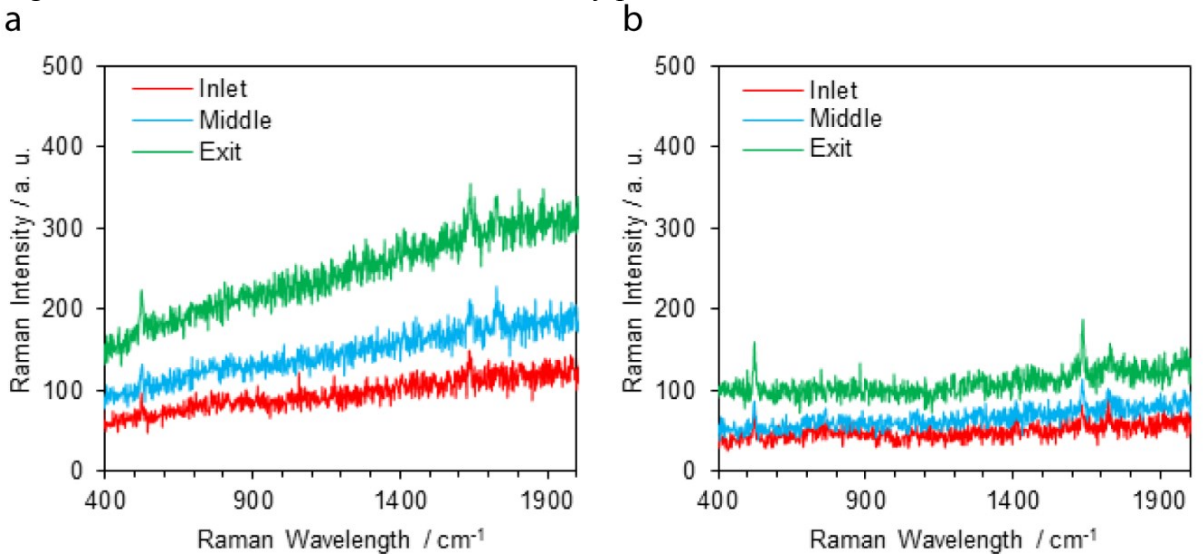
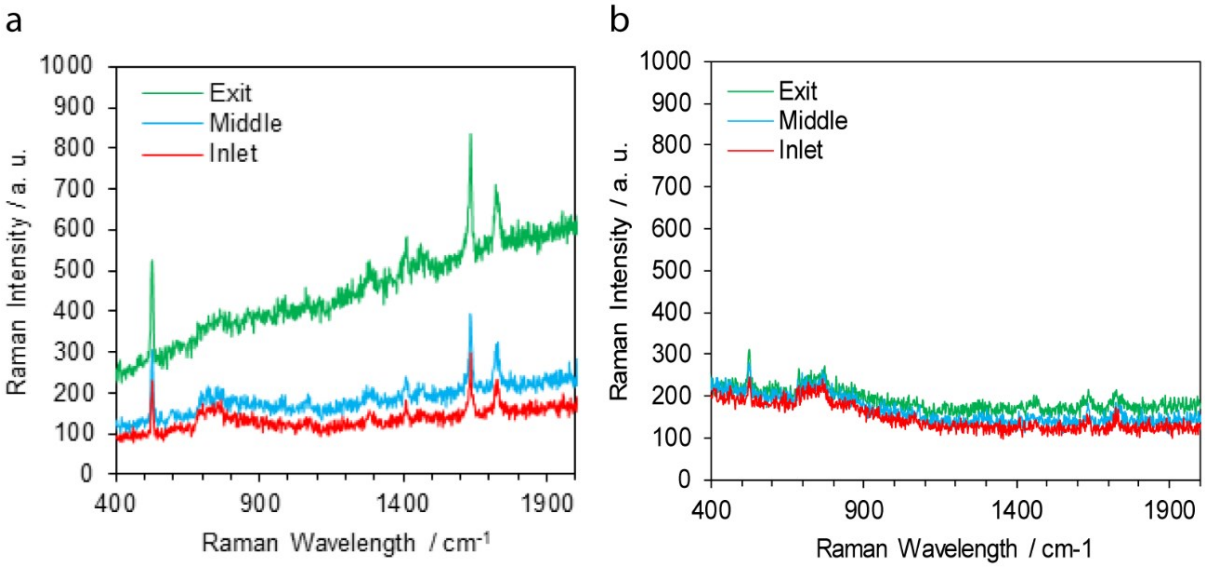


Figure S6: Representative Raman point scans of a sample (a) before and (b) after



polymerization over a period of 12 hours at an intensity of 4 mW/cm^2.

Figure S7: Representative Raman scans of a sample (a) before and (b) after polymerization over a period of 12 hours at an intensity of 20 mW/cm^2.

Degree of polymerization was calculated using Carother's equation[1] $N = \frac{2}{2-3p}$, where p corresponds to the total conversion. Degrees of polymerization achieved were 2.17 at 4 mW/cm^2 and 2.32 at 20 mW/cm^2 which are in close agreement with degrees of polymerization achieved in our previous work for a TMPTA based system[2]. Accordingly, the number average molecular weight was calculated using the equation $M_n = N * MW_{TMPTA}$. Radius of gyration of TMPTA was calculated using the equation[3] $< R_g^2 >= \frac{Nb^2}{6f}(3-2f)$ where N is 1, b is the end-to-end length of the TMPTA monomer, 1.44 nm and f is monomer functionality, i.e. 3.

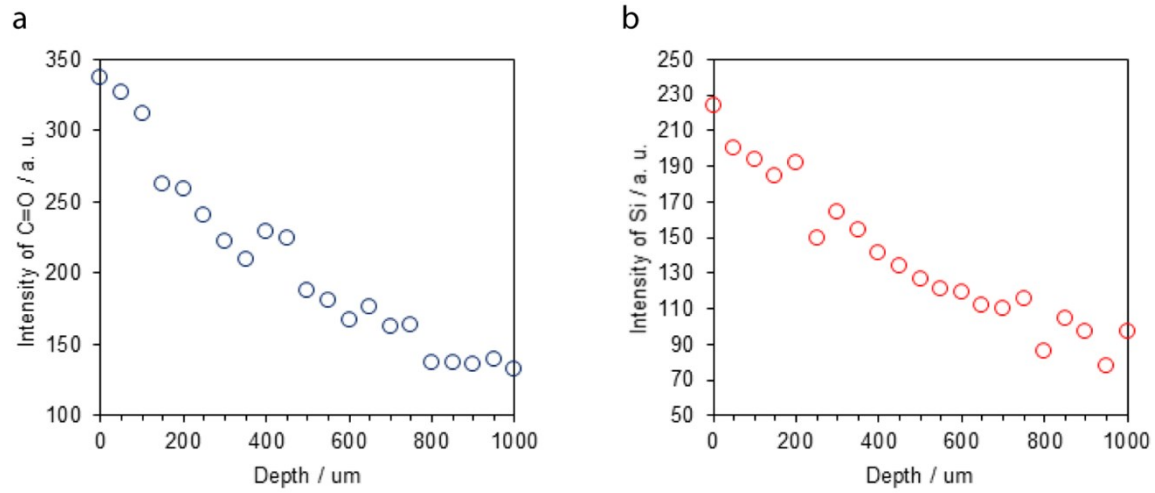


Figure S8: Depth scan of a sample before polymerization at 4 mW/cm^2.

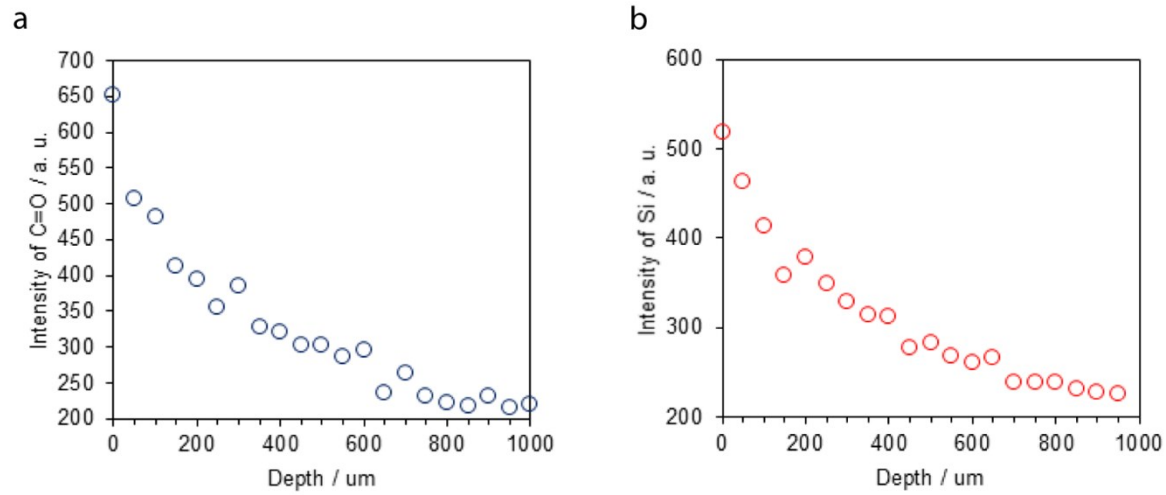


Figure S9: Depth scan of a sample before polymerization at 20 mW/cm^2.

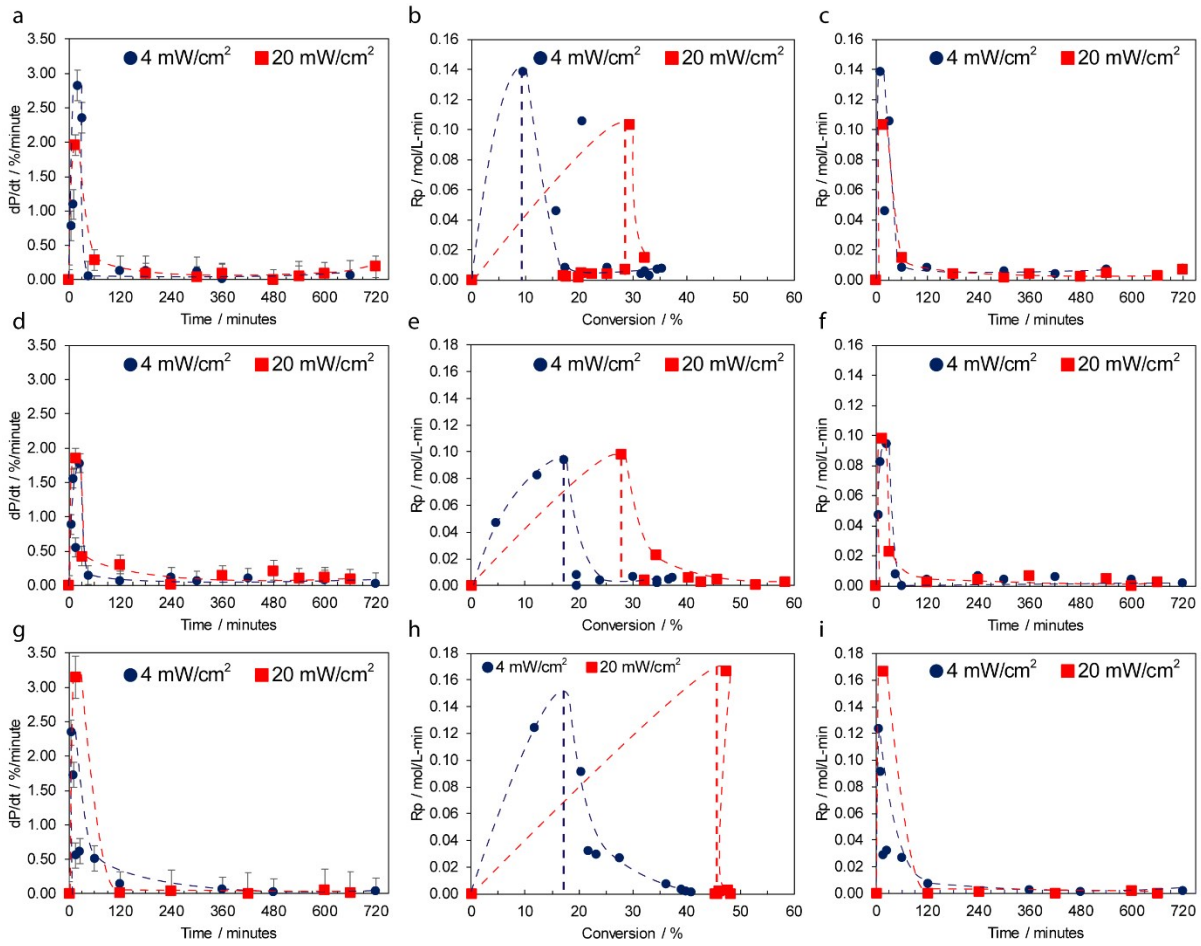


Figure S10: Kinetics data for (a-c) inlet, (d-f) middle and (g-i) exit faces of the sample.

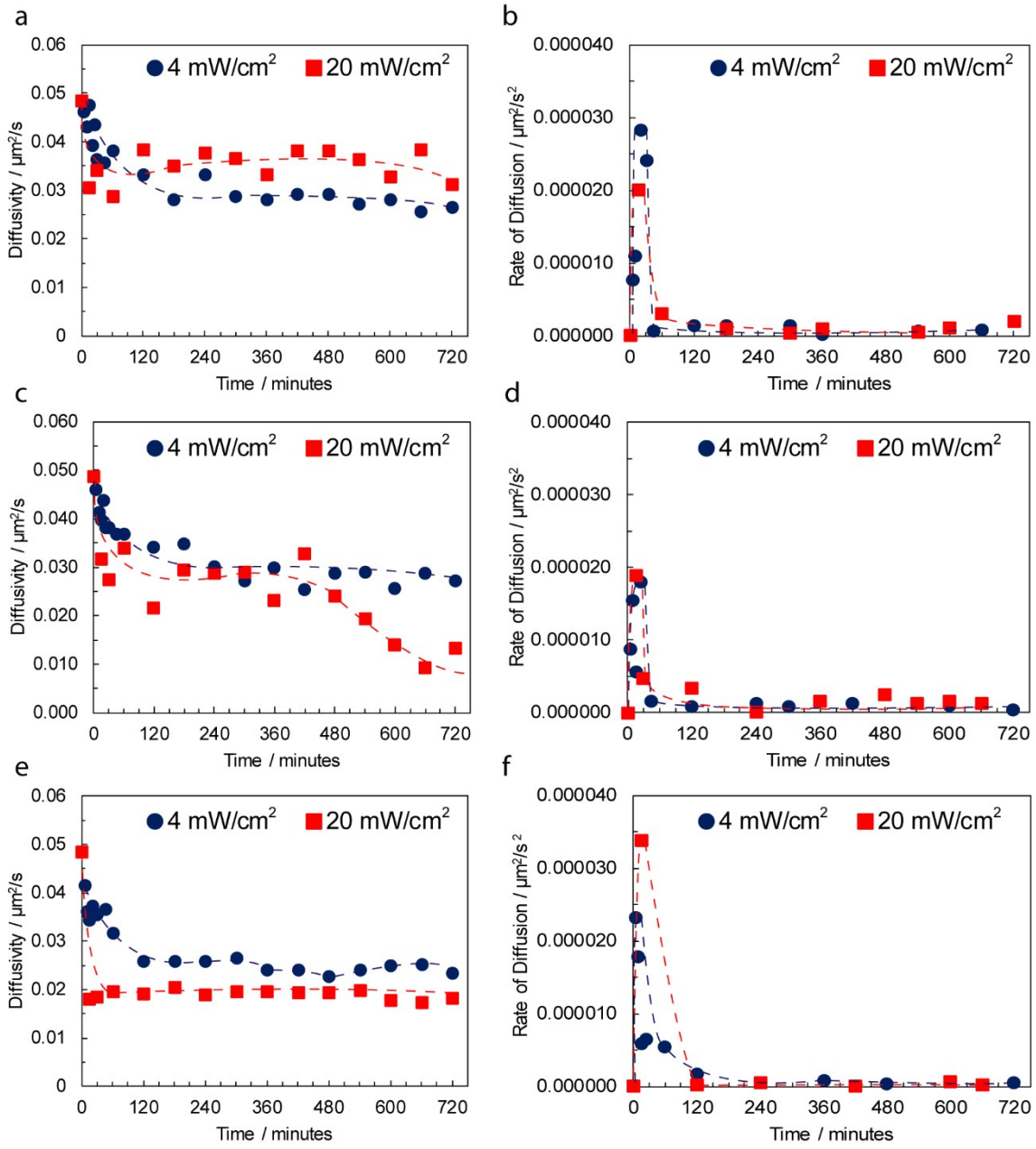


Figure S11: Diffusion data for (a-b) inlet, (c-d) middle and (e-f) exit faces of the sample.

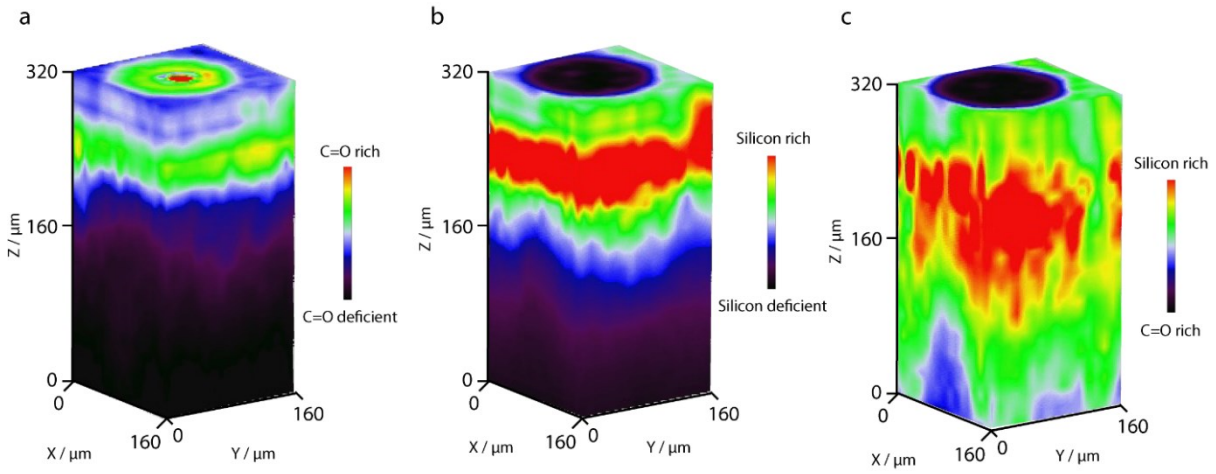


Figure S12: Full 3D Raman volume maps for a sample cured at 4 mW/cm^2.

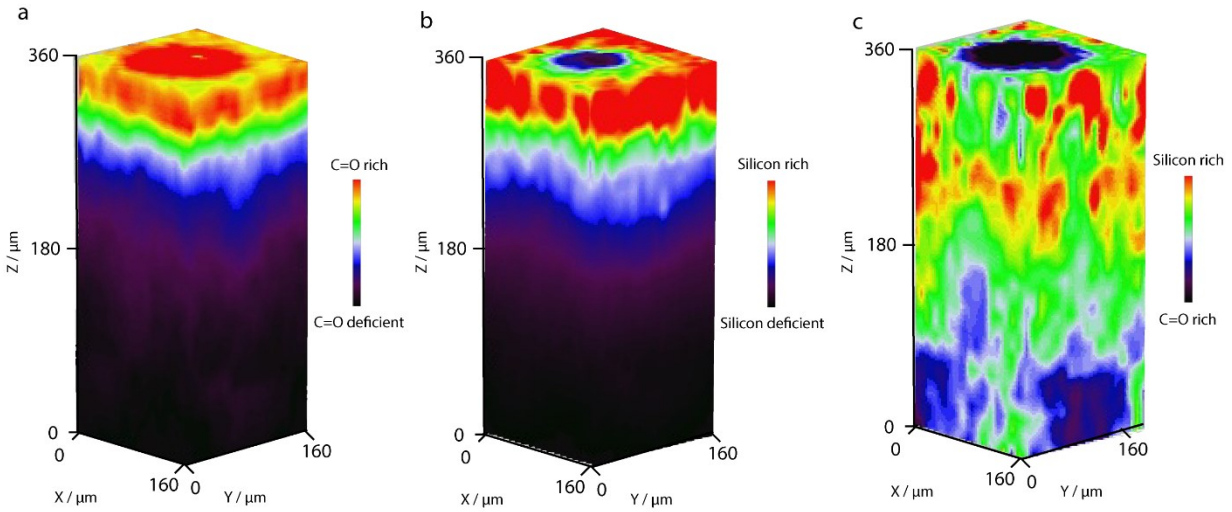


Figure S13: Full 3D Raman volume maps for a sample cured at 20 mW/cm^2.

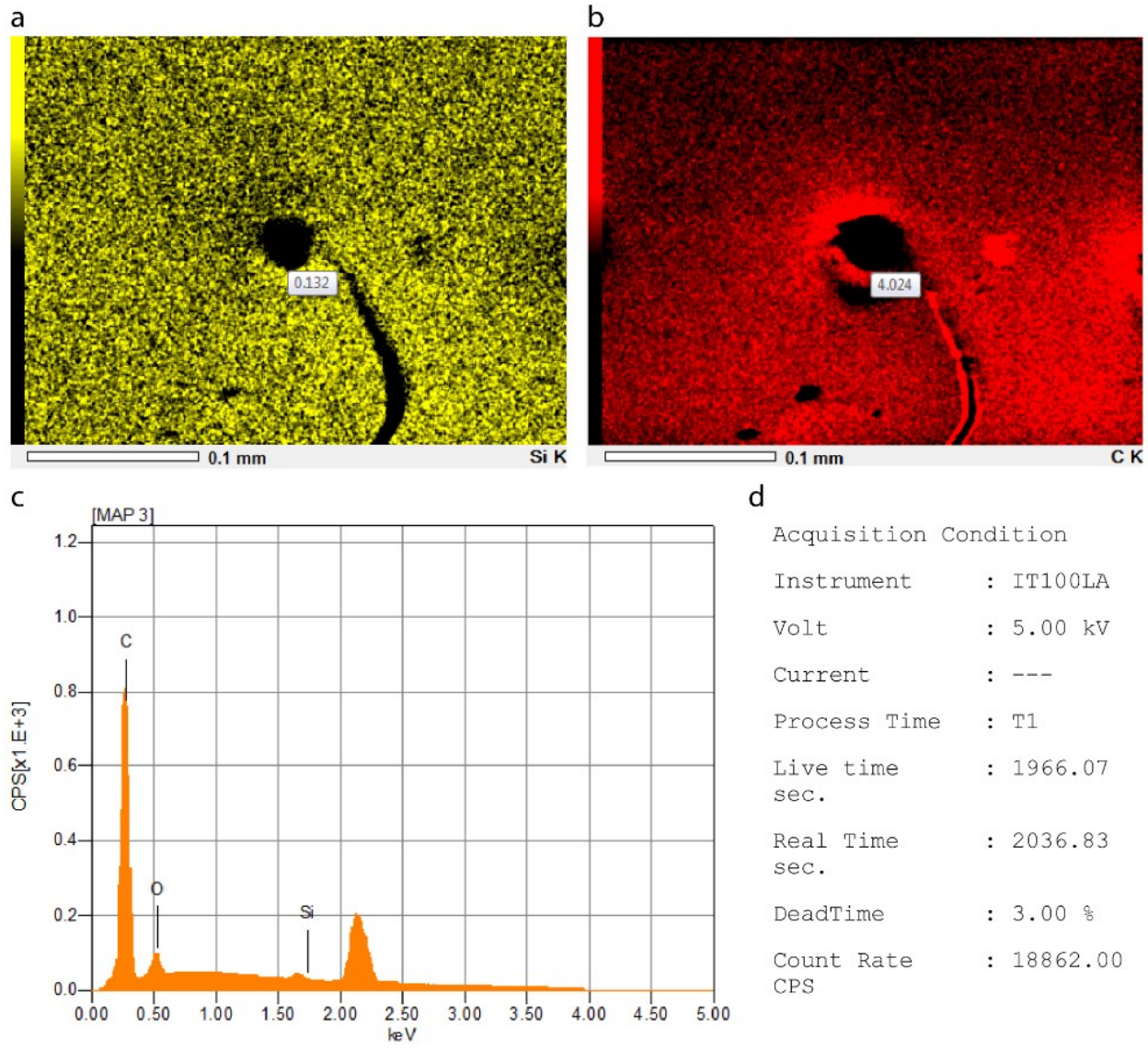


Figure S14: EDS map indicating local intensity at the center of the dark circular region for (a) Silicon and (b) Carbon, whereas (c) represents the EDS spectrum associated with the maps and (d) represents the acquisition conditions. The sample was cured at 4 mW/cm^2.

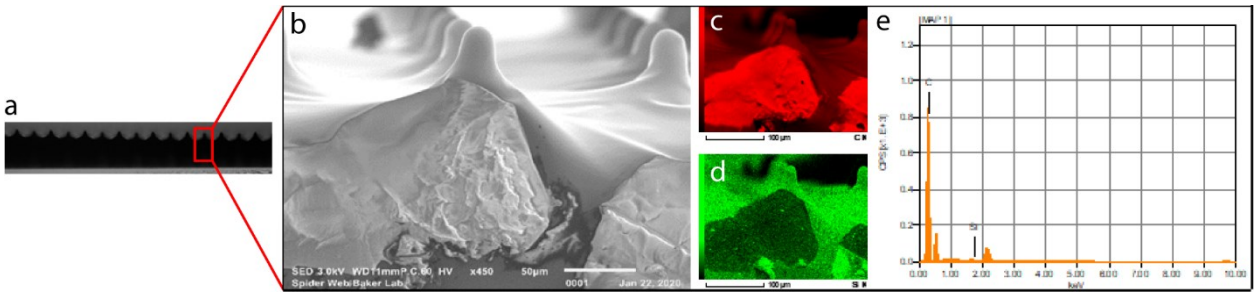


Figure S15: (a) Optical microscope image, (b) SEM image, and EDS maps of (c) Carbon and (d) Silicon acquired in cross-section for a sample cured at 4 mW/cm^2. (e) Represents the raw EDS spectrum associated with the EDS maps.

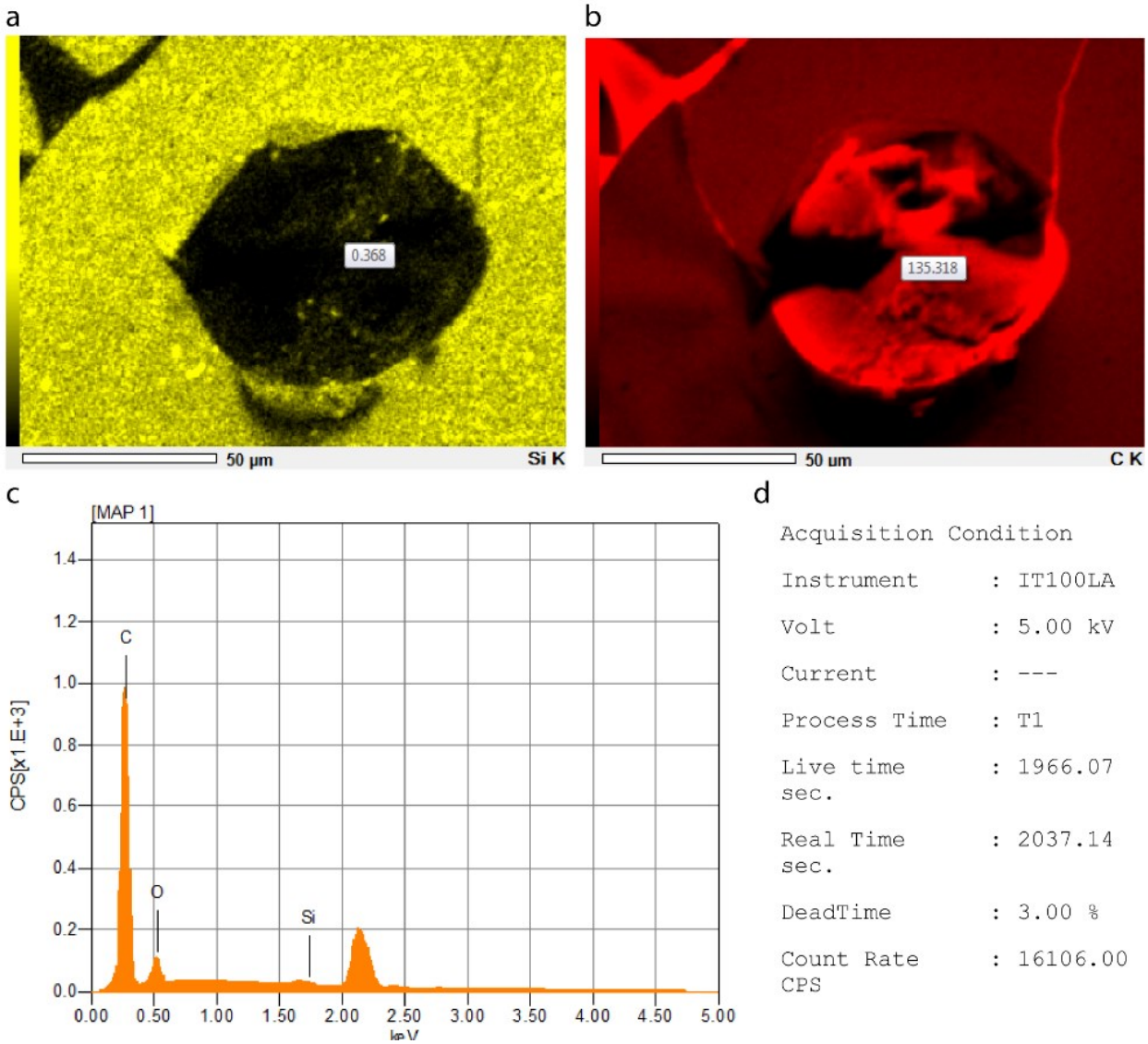


Figure S16: EDS map indicating local intensity at the center of the dark circular region for (a) Silicon and (b) Carbon, whereas (c) represents the EDS spectrum associated with the maps and (d) represents the acquisition conditions. The sample was cured at 20 mW/cm^2.

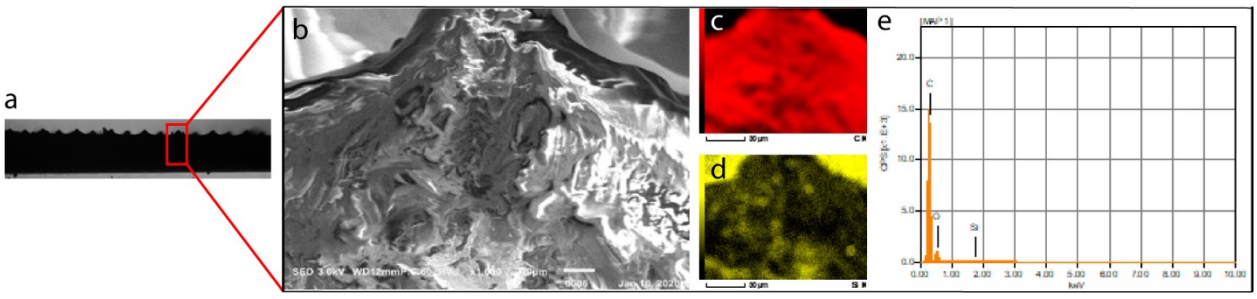


Figure S17: (a) Optical microscope image, (b) SEM image, and EDS maps of (c) Carbon and (d) Silicon acquired in cross-section for a sampled cured at 20 mW/cm^2. (e) Represents the raw EDS spectrum associated with the EDS maps.

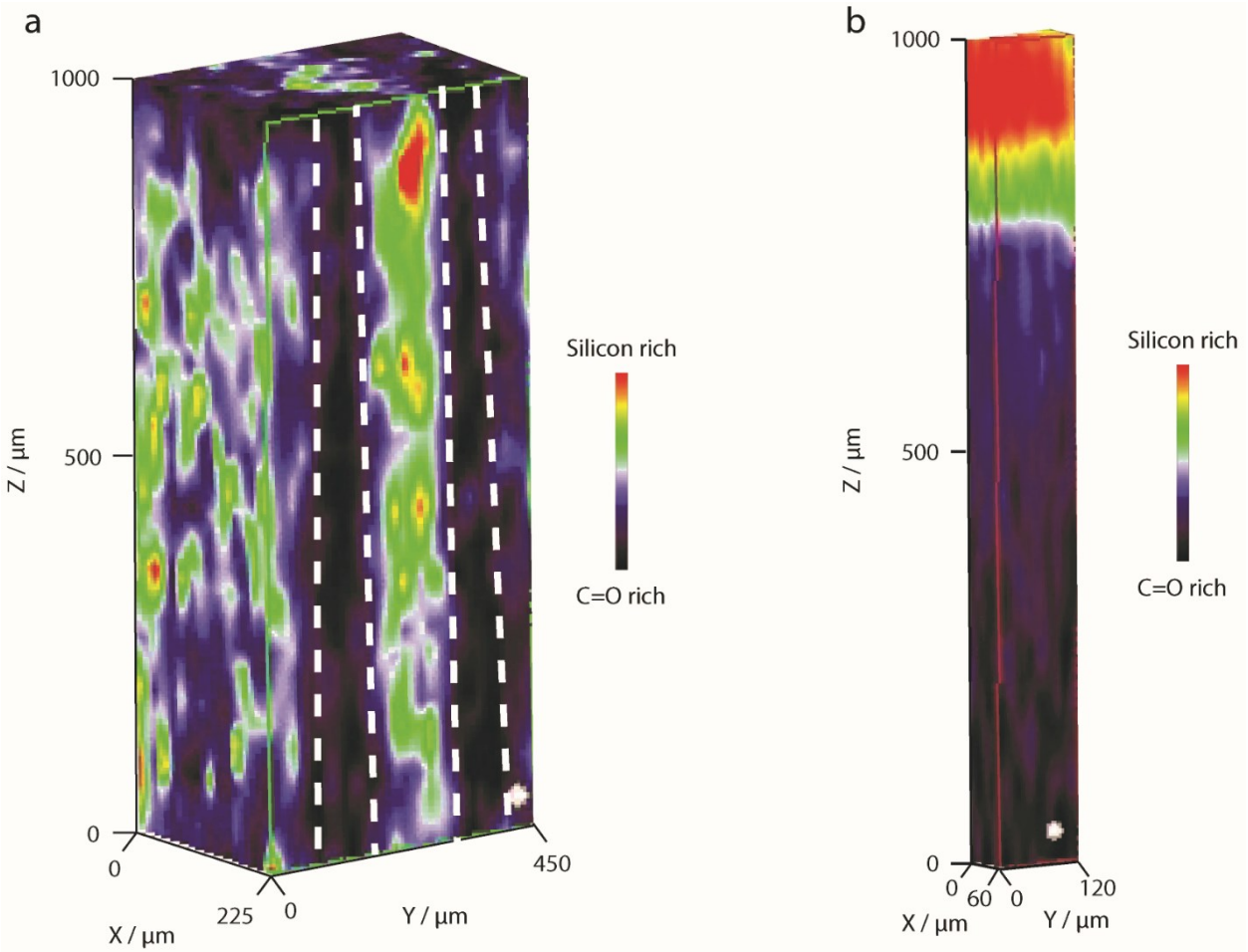


Figure S18: Cross-sectional 3D Raman volume maps of (a) a sample cured at 1.25 mW/cm^2 showing an exemplary phase-separated morphology and (b) a control experiment performed at 4 mW/cm^2 but without a photomask showing uniform curing over a large depth.

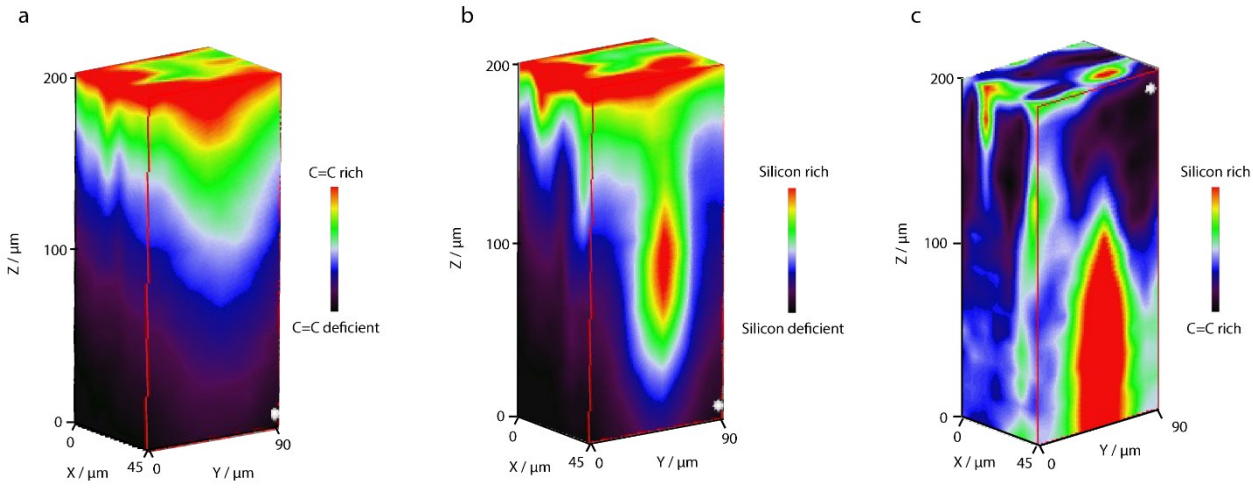


Figure S19: Cross-sectional 3D Raman volume maps of a sample cured using UV light for (a) TMPTA, (b) Silicon and (c) Silicon vs. TMPTA showing a Silicon rich core indicating the formation of an embedded morphology.

Table S1: Comparison of Silicon and Carbon EDS intensities for samples cured at 4 mW/cm^2 and 20 mW/cm^2 obtained from EDS maps shown in figures S14(a-b) and S16(a-b), respectively.

Curing Condition	Si intensity at center (a. u.)	C intensity at center (a. u.)
4 mW/cm^2, 24 hours	0.132	4.024
20 mW/cm^2, 4 hours	0.368	135.318

Estimation of solution viscosity using the Einstein relation[4]: $\eta = \eta_0(1 + 2.5\phi)$

Volume fraction of Silicon in the sample (ϕ) = 0.000455

Bulk viscosity of TMPTA (η_0, kg/m-s) = 0.1

Therefore, initial bulk viscosity of the sample before polymerization (η, kg/m-s) = 0.10011375

Relative viscosity $\eta_{Rel} = \frac{\eta}{\eta_0}$ = 1.0011375

Estimation of intrinsic viscosity using the Billmeyer relation[5]: $0.25\frac{(\eta_{Rel} - 1) + 3\ln(\eta_{Rel})}{c}$

Where c (g/dL) is the mass concentration of Silicon, i.e. 0.106

Therefore, the initial intrinsic viscosity of the sample corresponding to the initial bulk viscosity ([η], dL/g) = 0.0107265

Estimation of intrinsic viscosity using the Solomon-Ciuta relation[6]: $\frac{\sqrt{2(\eta_{Rel} - 1 - \ln(\eta_{Rel})}}{c}$

Therefore, initial intrinsic viscosity calculated using this relation (dL/g) = 0.0107255

Ratio between initial bulk viscosity and initial intrinsic viscosity = 9.33

Estimation of the Mark-Houwink parameter 'K' (assuming $M_v = M_w$): $K = \frac{[\eta]}{M^a}$

Molar mass of TMPTA (M, g/mol) = 296.32

Assumed exponent 'a' = 0.8

Therefore, calculated valued of K (dL/g) = 0.000112993

The Mark-Houwink equation[7] was then used to reverse calculate intrinsic viscosities as a function of polymer molecular weight. The factor of 9.33 was used to convert each intrinsic viscosity to bulk viscosity followed by estimation of diffusion coefficients.

Time (min)	Conversion (%)	N	MW (g/mol)	Viscosity (Pa-s)	Diffusion Coefficient ($\mu m^2/s$)
0	0	1	296.32	0.1	0.0485
5	4.4	1.071	317.46	0.105	0.0458
10	12.2	1.224	362.84	0.117	0.0412
15	14.9	1.290	382.35	0.122	0.0395
20	8.3	1.143	338.65	0.111	0.0435
25	17.2	1.348	399.53	0.127	0.0382
30	17.2	1.348	399.53	0.127	0.0381
45	19.4	1.411	418.33	0.131	0.0368
60	19.4	1.412	418.33	0.132	0.0368
120	23.8	1.558	461.80	0.143	0.0340
180	22.7	1.519	450.11	0.139	0.0347
240	29.9	1.818	538.76	0.161	0.0300
300	34.4	2.069	613.07	0.178	0.0271
360	30.5	1.846	547.05	0.163	0.0296
420	37.2	2.264	670.91	0.192	0.0252
480	32.2	1.935	573.52	0.169	0.0285
540	31.6	1.905	564.42	0.167	0.0289
600	36.6	2.222	658.48	0.189	0.0255
660	32.2	1.935	573.52	0.169	0.0285
720	34.4	2.069	613.07	0.178	0.027

Table S2: Representative values of monomer conversion, degree of conversion *N*, molecular weight, intrinsic viscosity and diffusion coefficient over time for 4 mW/cm^2 in the middle of a channel.

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[3] Rubinstein, M.; Colby, R. H., Polymer Physics. Oxford University Press New York 2003; 23.

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[7] Hiemenz, P. C., & Lodge, T. P. (2007). Polymer chemistry. CRC press.