Supporting Information.

3D Photoinduced Spatiotemporal Resolution of Cellulose-based Hydrogels for Fabrication of Biomedical Devices

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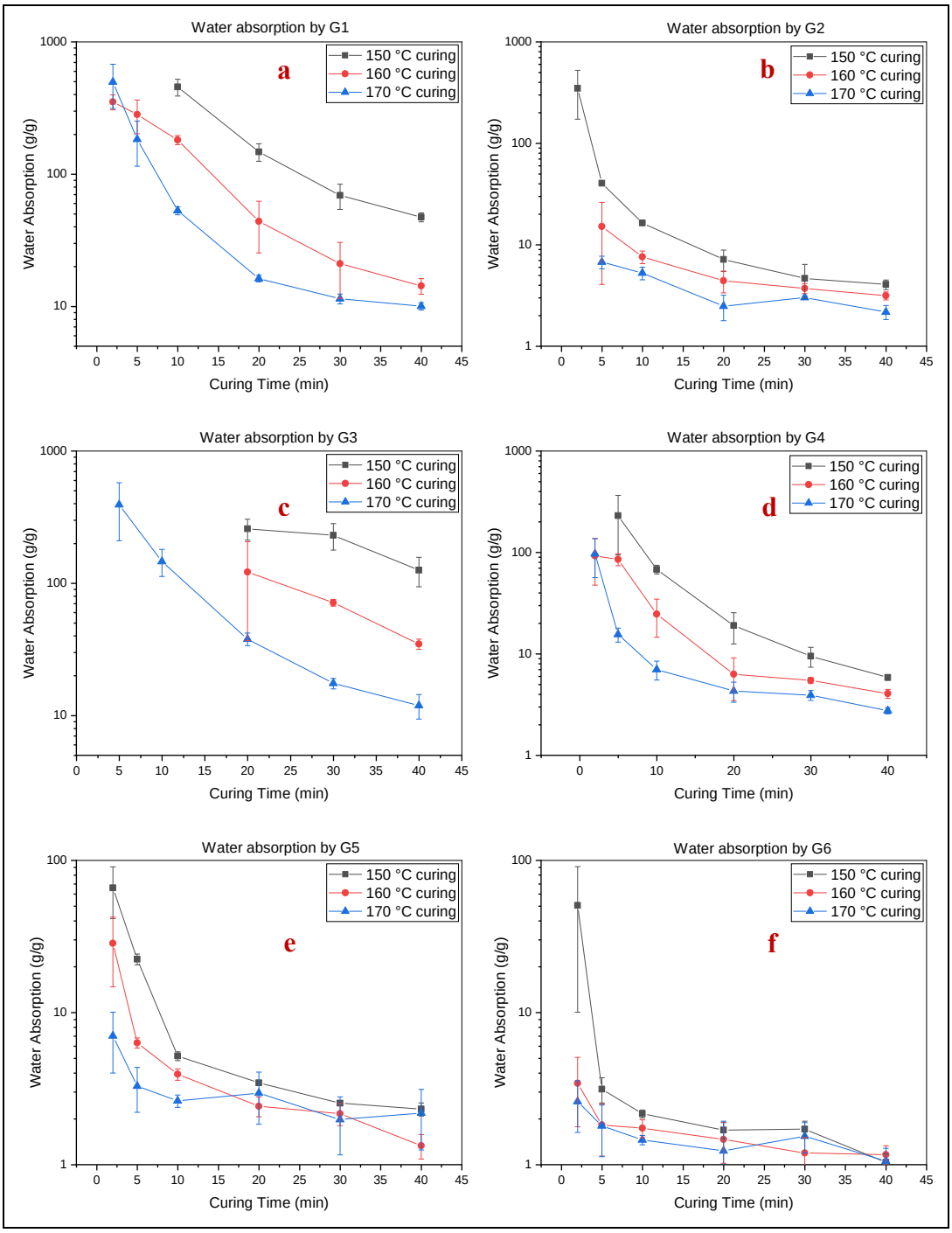

Figure S1: Swelling data for gels due to water absorption. The effect of different molecular weights of CMC, amount of crosslinker (Citric Acid) and curing conditions. Missing points in graph are due to disintegrated gels. Films - a) G1, b) G2, c) G3, d) G4, e) G5, f) G6.

Table S1 : XPS carbon (C 1s) and oxygen (O 1s) bonding percentages for various samples.

G7	G5 L20 cured at 160 °C for 30 min	G5 L20	G5 cured at 160 °C for 30 min	G5	Riboflavin Powder	Citric Acid Powder	CMC (250k Da) Film	CMC (250k Da) Powder	Code	C-O bond (C-N in Riboflavin)	Approx. BE (eV)
0	0	9	0	0	0	0	0	14	$C1_x$	C=C	**283.7**
21	41	37	18	32	33	36	18	63	$C2_x$	C-C / C-H	**284.8**
54	41	37	55	45	47	17	56	16	$C3_x$	C-O / C-N	**286.6**
17	13	12	18	16	8	0	21	4	$C4_x$	O-C-O / C=O / N-C=N	**288.2**
6	2	4	6	5	10	47	2	3	$C5_x$	O-C=O / N-C=O	**289.3**
2	3	1	3	2	2	0	3	0	$C6_x$	O-CO=O / N-CN=O	**291**
0	0	0	0	0	0	0	0	10	$O1_x$	Na-O	**528.9**
24	8*	9	17	16	26	0	23	21*	$O2_x$	O=C	**531.2**
46	34*	35	20	19	0	44	47	44*	$O3_x$	O=C-O	**532**
27	33*	12	47	48	72	24	31	25*	$O4_x$	O-C	**533**
3	24*	44	16	16	2	32	0	0	$O5_x$	O-C=O	**533.6**

Approx. BE (eV)	C-O bond (C-N in Riboflavin)	Code	G7 L20 cured at 160 °C for 30 min	G7 L20	G7 cured at 160 °C for 30 min
283.7	C=C	$C1_x$	0	0	0
284.8	C-C / C-H	$C2_x$	36	33	22
286.6	C-O / C-N	$C3_x$	43	46	54
288.2	O-C-O / C=O / N-C=N	$C4_x$	15	15	16
289.3	O-C=O / N-C=O	$C5_x$	4	4	6
291	O-CO=O / N-CN=O	$C6_x$	3	2	2
528.9	Na-O	$O1_x$	0	0	0
531.2	O=C	$O2_x$	25	21	18
532	O=C-O	$O3_x$	31	26	28
533	O-C	$O4_x$	37	45	39
533.6	O-C=O	$O5_x$	8	8	14

* Binding energy was lower by about 1eV

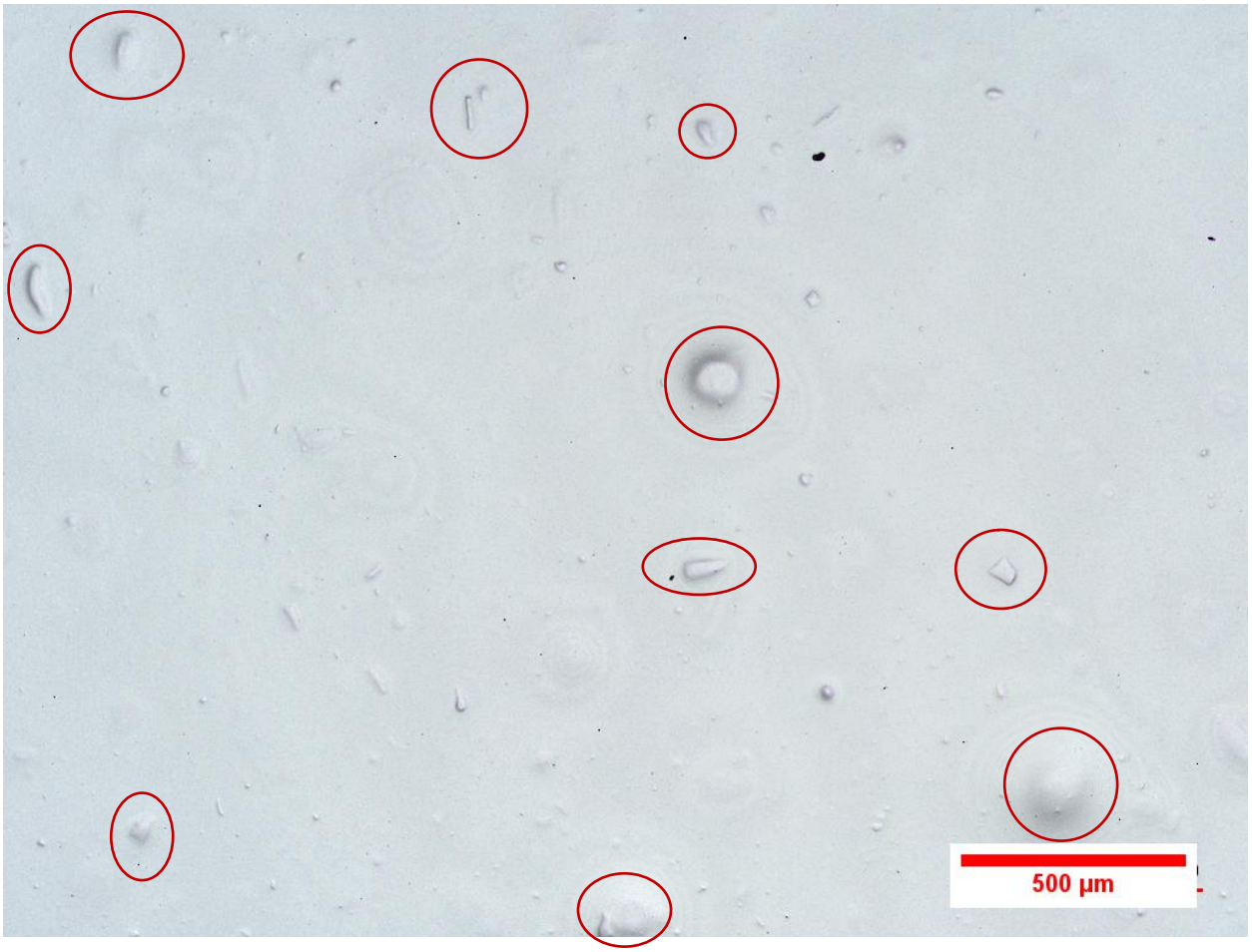

Figure S2: Laser microscopy of G5 film (5x magnification) (no ammonium hydroxide treatment before film casting). CMC aggregates marked with red circles and ellipses.

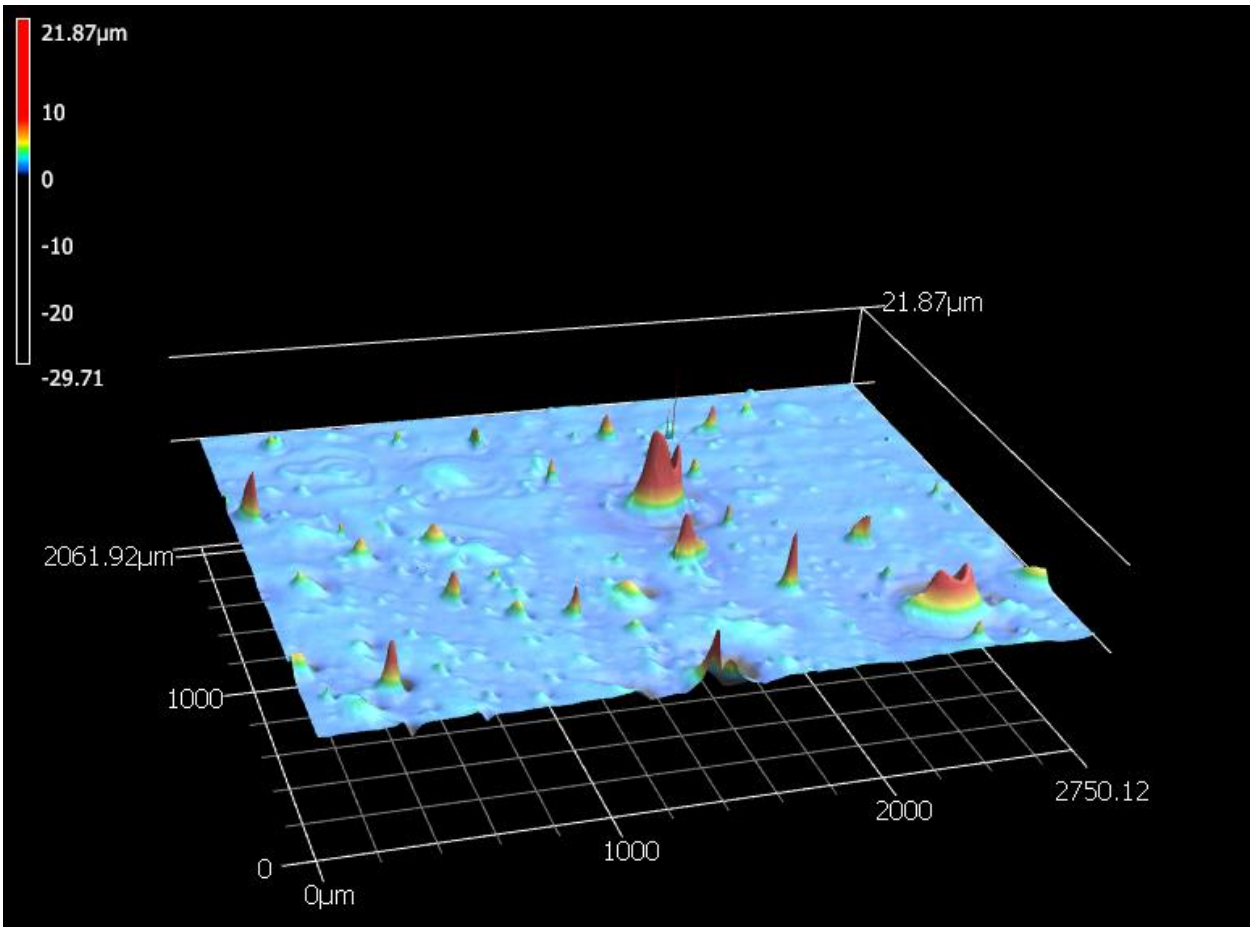

Figure S3: 3D surface plot of G5 film (no ammonia treatment before film casting). Ref. Figure S2

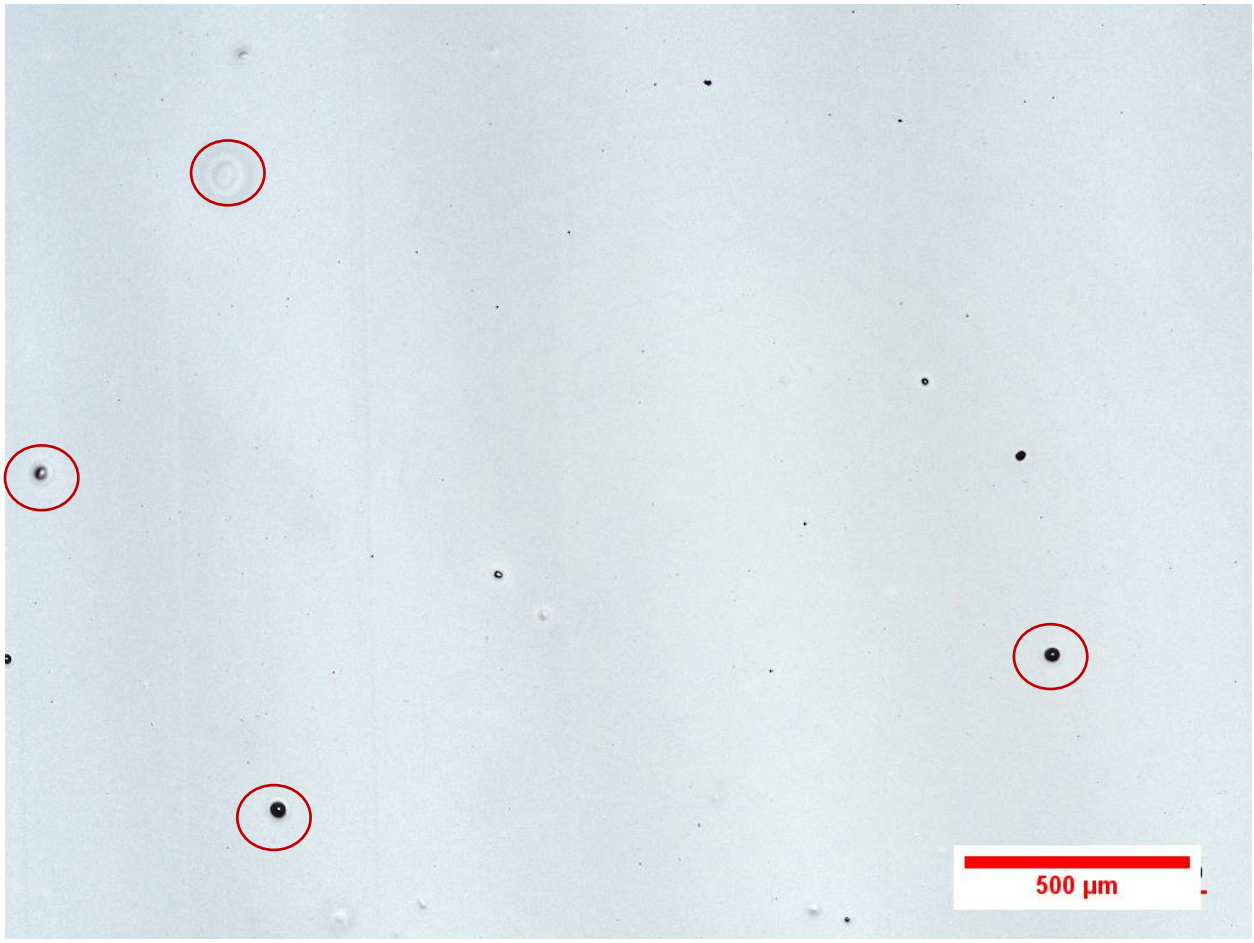

Figure S4: Laser microscopy of G5 film (5x magnification) (CMC treated with ammonium hydroxide solution before film casting). CMC aggregates marked with red circles and ellipses.

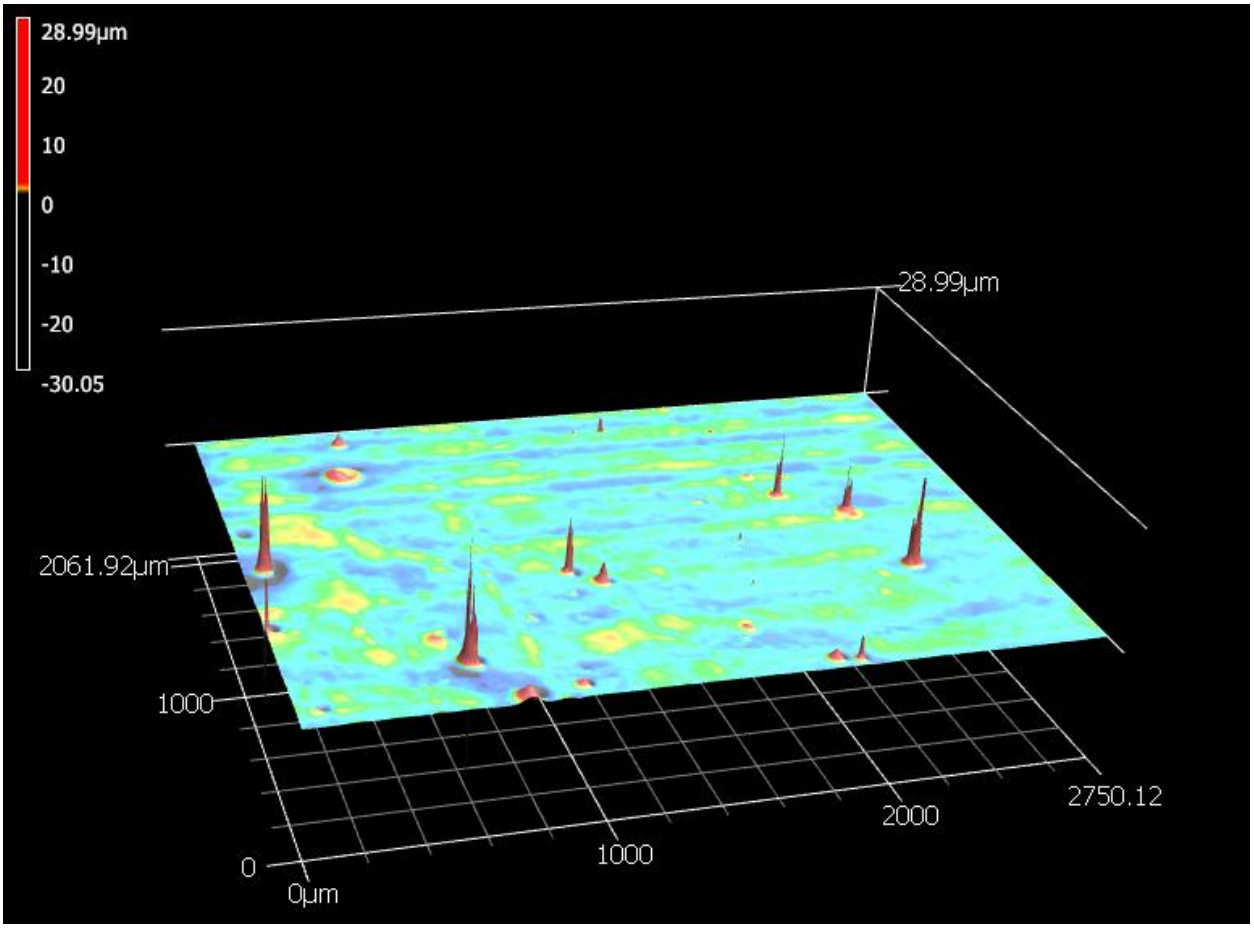

Figure S5: 3D surface plot of G5 film (CMC treated with ammonium hydroxide solution before film casting). Ref. Figure S4

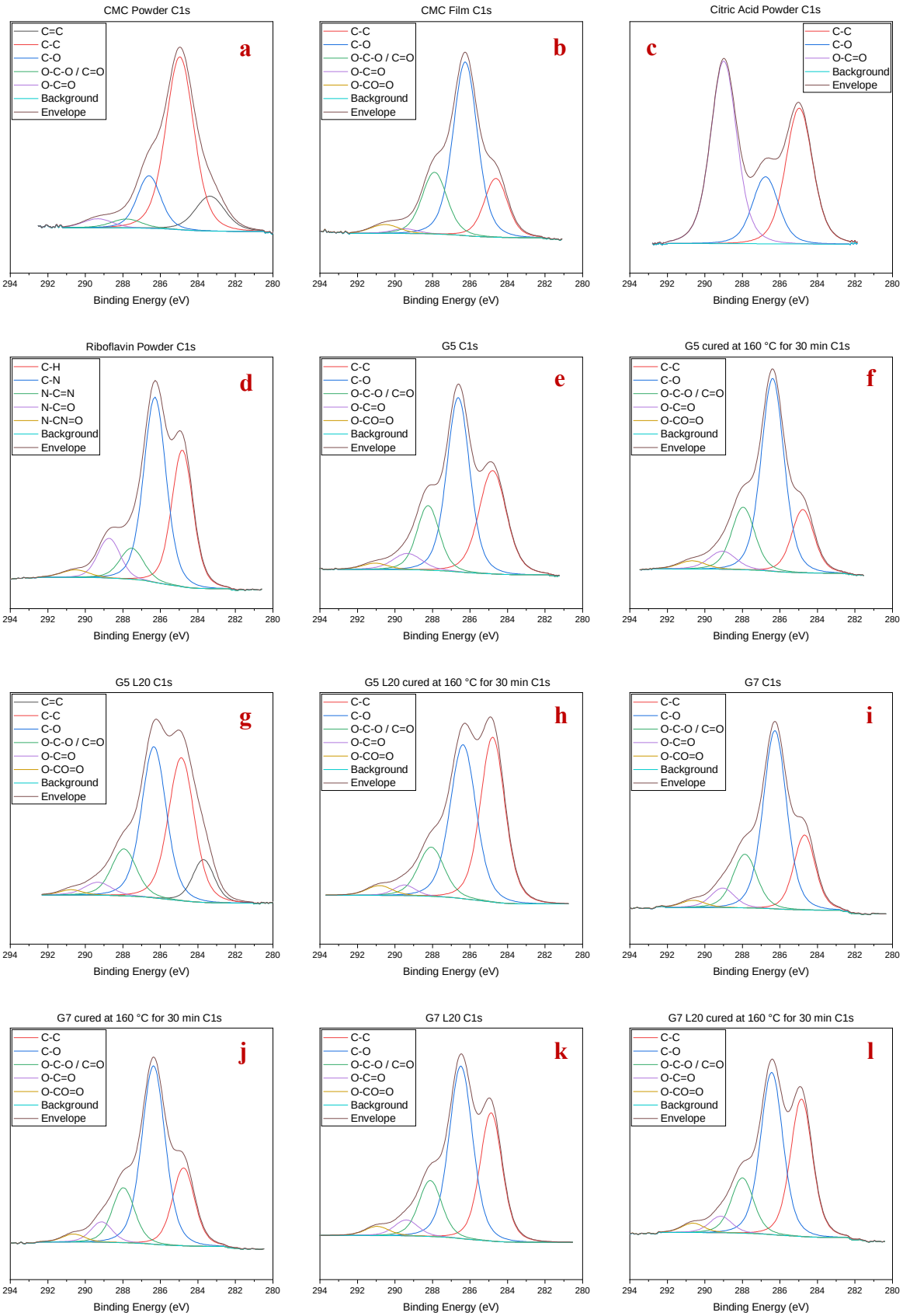
CMC Powder C1s
a
C=C
C-C
C-O
O-C-O / C=O
O-C=O
Background
Envelope
CMC Film C1s
b
C-C
C-O
O-C-O / C=O
O-C=O
O-CO=O
Background
Envelope
Citric Acid Powder C1s
c
C-C
C-O
O-C=O
Background
Envelope
Riboflavin Powder C1s
d
C-H
C-N
N-C=N
N-C=O
N-CN=O
Background
Envelope
G5 C1s
e
C-C
C-O
O-C-O / C=O
O-C=O
O-CO=O
Background
Envelope
G5 cured at 160 °C for 30 min C1s
f
C-C
C-O
O-C-O / C=O
O-C=O
O-CO=O
Background
Envelope
G5 L20 C1s
g
C=C
C-C
C-O
O-C-O / C=O
O-C=O
O-CO=O
Background
Envelope
G5 L20 cured at 160 °C for 30 min C1s
h
C-C
C-O
O-C-O / C=O
O-C=O
O-CO=O
Background
Envelope
G7 C1s
i
C-C
C-O
O-C-O / C=O
O-C=O
O-CO=O
Background
Envelope
G7 cured at 160 °C for 30 min C1s
j
C-C
C-O
O-C-O / C=O
O-C=O
O-CO=O
Background
Envelope
G7 L20 C1s
k
C-C
C-O
O-C-O / C=O
O-C=O
O-CO=O
Background
Envelope
G7 L20 cured at 160 °C for 30 min C1s
l
C-C
C-O
O-C-O / C=O
O-C=O
O-CO=O
Background
Envelope
294 292 290 288 286 284 282 280
Binding Energy (eV)

Figure S6: De-convoluted C1s XPS spectra for samples measured in the study. a) CMC Powder, b) CMC film, c) Citric acid powder, d) Riboflavin powder, e) G5 film (uncured), f) G5 film (cured), g) G5 film laser ablated (uncured), h) G5 film laser ablated (cured), i) G7 film (uncured), j) G7 film (cured), k) G7 film laser ablated (uncured), l) G7 film laser ablated (cured).

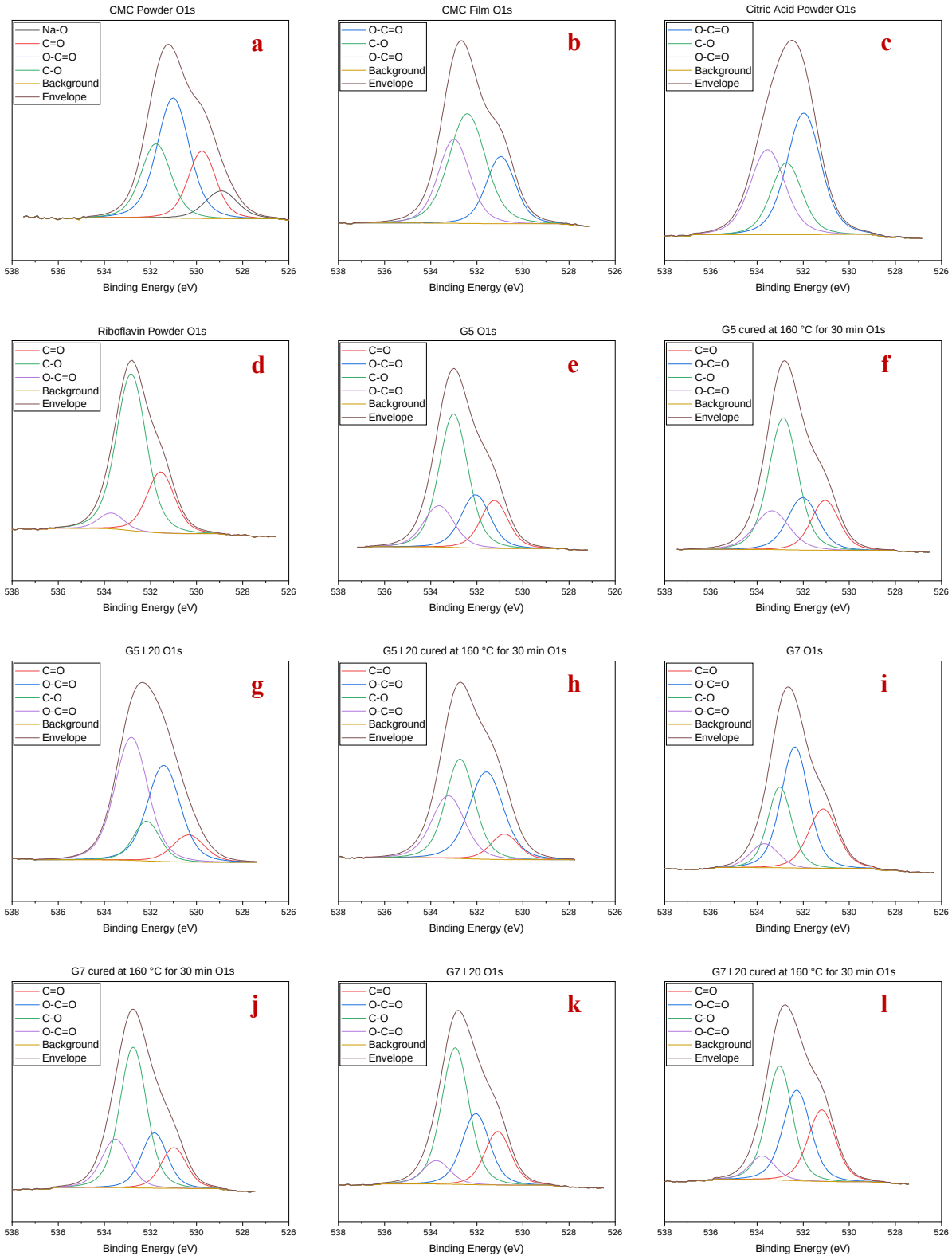
CMC Powder O1s
Na-O
C=O
O-C=O
C-O
Background
Envelope
a
CMC Film O1s
O-C=O
C-O
O-C=O
Background
Envelope
b
Citric Acid Powder O1s
O-C=O
C-O
O-C=O
Background
Envelope
c
Riboflavin Powder O1s
C=O
C-O
O-C=O
Background
Envelope
d
G5 O1s
C=O
O-C=O
C-O
O-C=O
Background
Envelope
e
G5 cured at 160 °C for 30 min O1s
C=O
O-C=O
C-O
O-C=O
Background
Envelope
f
G5 L20 O1s
C=O
O-C=O
C-O
O-C=O
Background
Envelope
g
G5 L20 cured at 160 °C for 30 min O1s
C=O
O-C=O
C-O
O-C=O
Background
Envelope
h
G7 O1s
C=O
O-C=O
C-O
O-C=O
Background
Envelope
i
G7 cured at 160 °C for 30 min O1s
C=O
O-C=O
C-O
O-C=O
Background
Envelope
j
G7 L20 O1s
C=O
O-C=O
C-O
O-C=O
Background
Envelope
k
G7 L20 cured at 160 °C for 30 min O1s
C=O
O-C=O
C-O
O-C=O
Background
Envelope
l
538 536 534 532 530 528 526
Binding Energy (eV)

Figure S7: De-convoluted O1s XPS spectra of samples measured in this study. a) CMC Powder, b) CMC film, c) Citric acid powder, d) Riboflavin powder, e) G5 film (uncured), f) G5 film (cured), g) G5 film laser ablated (uncured), h) G5 film laser ablated (cured), i) G7 film (uncured), j) G7 film (cured), k) G7 film laser ablated (uncured), l) G7 film laser ablated (cured).

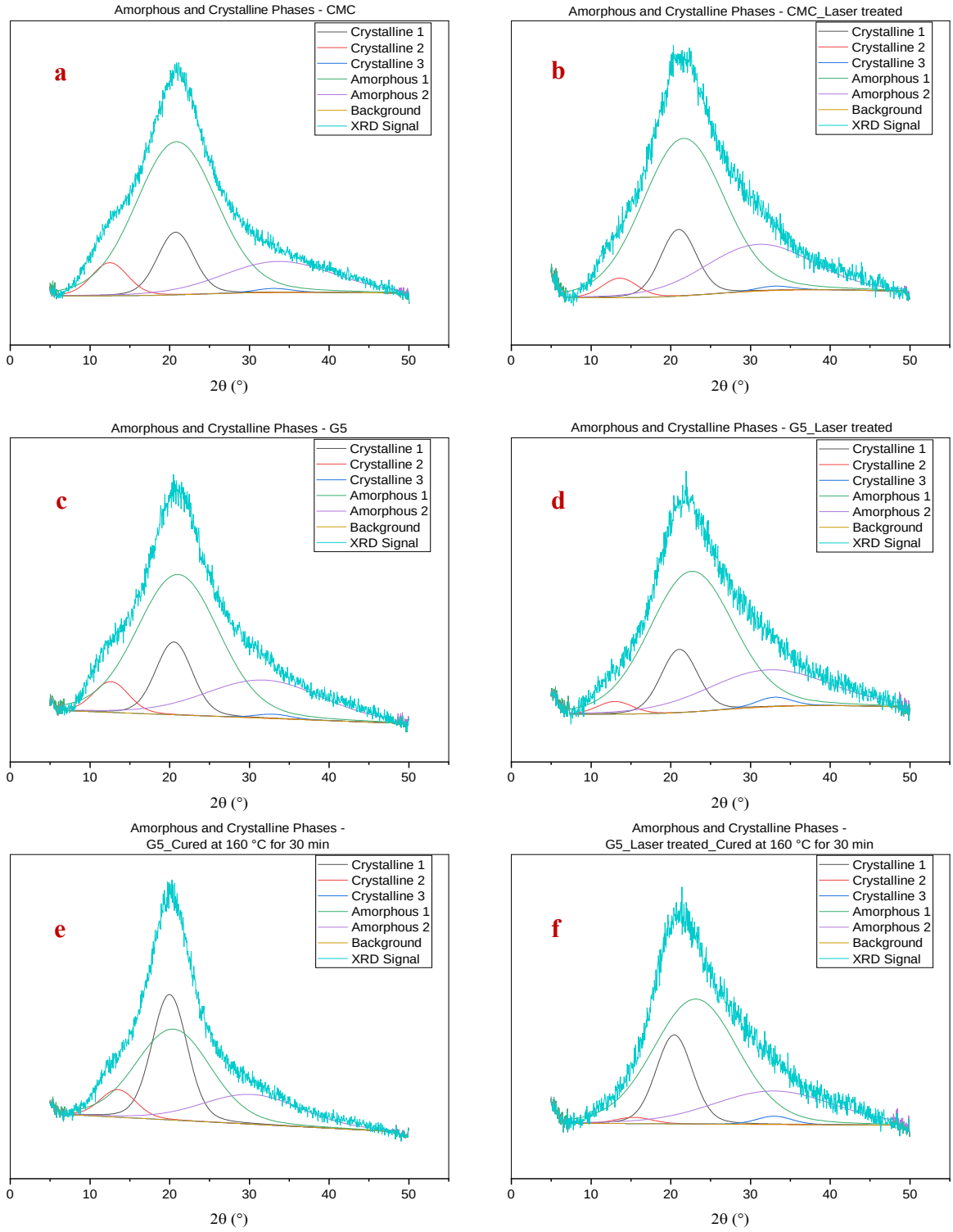
Amorphous and Crystalline Phases - CMC
a
Crystalline 1
Crystalline 2
Crystalline 3
Amorphous 1
Amorphous 2
Background
XRD Signal
0
10
20
30
40
50
2θ (°)
Amorphous and Crystalline Phases - CMC_Laser treated
b
Crystalline 1
Crystalline 2
Crystalline 3
Amorphous 1
Amorphous 2
Background
XRD Signal
0
10
20
30
40
50
2θ (°)
Amorphous and Crystalline Phases - G5
c
Crystalline 1
Crystalline 2
Crystalline 3
Amorphous 1
Amorphous 2
Background
XRD Signal
0
10
20
30
40
50
2θ (°)
Amorphous and Crystalline Phases - G5_Laser treated
d
Crystalline 1
Crystalline 2
Crystalline 3
Amorphous 1
Amorphous 2
Background
XRD Signal
0
10
20
30
40
50
2θ (°)
Amorphous and Crystalline Phases -
G5_Cured at 160 °C for 30 min
e
Crystalline 1
Crystalline 2
Crystalline 3
Amorphous 1
Amorphous 2
Background
XRD Signal
0
10
20
30
40
50
2θ (°)
Amorphous and Crystalline Phases -
G5_Laser treated_Cured at 160 °C for 30 min
f
Crystalline 1
Crystalline 2
Crystalline 3
Amorphous 1
Amorphous 2
Background
XRD Signal
0
10
20
30
40
50
2θ (°)

Figure S8: XRD deconvolutions for CMC films and G5 films before and after laser treatment and curing at 160 °C for 30 min (160/30). a) CMC film, b) CMC film after laser ablation, c) G5 film, d) G5 film after laser ablation, e) G5 film after curing, f) G5 film after laser exposure and curing.