

Cationic surfactant-directed structural control of NaCl crystals from evaporating sessile droplets

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Electronic Supplementary Information (ESI)

Table S1

Sample	Concentration	Solution Viscosity (mPa.s) at temperature 24°C
1	0.1M NaCl + 0.0001M CTAB	1.02
2	0.1M NaCl + 0.001M CTAB	1.05
3	0.1M NaCl + 0.01M CTAB	1.07
4	0.1M NaCl + 0.02M CTAB	1.08
5	0.1M NaCl + 0.1M CTAB	1.15
6	0.5M NaCl + 0.0001M CTAB	1.06
7	0.5M NaCl + 0.001M CTAB	1.07
8	0.5M NaCl + 0.01M CTAB	1.11
9	0.5M NaCl + 0.02M CTAB	1.17
10	0.5M NaCl + 0.1M CTAB	1.32
11	2M NaCl + 0.0001M CTAB	1.19
12	2M NaCl + 0.001M CTAB	1.20
13	2M NaCl + 0.01M CTAB	1.22
14	2M NaCl + 0.02M CTAB	1.36
15	2M NaCl + 0.1M CTAB	1.58
16	Only CTAB_0.0001M	1.01
17	Only CTAB_0.01M	1.04
18	Only CTAB_0.1M	1.14

Table S2

Concentrations of CTAB (C_{CTAB} in (M)), Equilibrium contact angle, Droplet pinning time (t_P), Crystallisation time (t_C), their difference (t_C-t_P), Solidification time (t_S), and Intrinsic contact angle of droplet at time of pinning (θ_{iP}). All the data are obtained for a constant $C_{NaCl} = 0.1$ (M).

C_{CTAB} (M)	$\theta_{Eqm.} (^\circ)$	t_P (min)	t_C (min)	t_S (min)	t_C-t_P (min)	$\theta_{iP} (^\circ)$
0.0001	53.39	10.22	16.4	6.53	6.18	13.57
0.001	52.12	9.02	22	6.94	12.98	17.6
0.01	46.79	6.2	23.06	14.14	16.86	20.38
0.02	26.67	1.06	23	16.27	21.94	22
0.1	25.33	0.5	24.2	57.1	23.7	25

The characteristics of surfactant-containing inorganic salt solutions are controlled by the total molality of the mixture m , which can be expressed in the following way

$$m = 2m_1 + 2m_2 \quad (1)$$

Where m_1 and m_2 are the molalities of NaCl and CTAB, respectively. In aqueous solutions, NaCl and CTAB dissociate into ions. Mole fractions (x_1 and x_2) of NaCl and CTAB can be given as

$$(x_1) = \frac{2m_1}{m} = \frac{m_1}{(m_1 + m_2)} \quad (2)$$

$$(x_2) = \frac{2m_2}{m} = \frac{m_2}{(m_1 + m_2)} \quad (3)$$

The values of m_1 , m_2 , x_1 and x_2 for different surfactant concentrations containing 0.1 (M) NaCl solution are calculated and given in Table S1. Similarly, Table S2 and S3 are followed for 0.5 (M) and 2 (M) NaCl solutions, respectively.

Table S3

C_{NaCl} (M)	0.1	0.1	0.1	0.1	0.1
C_{CTAB}	0.1	0.02	0.01	0.001	0.0001
m	0.4	0.24	0.22	0.202	0.2002
x_1	0.5	0.833	0.909	0.990	0.9990
x_2	0.5	0.167	0.0909	0.0099	0.0009

Table S4

Concentrations of CTAB (C_{CTAB} in (M)), Equilibrium contact angle, Droplet pinning time (t_p), Droplet crystallisation time (t_c), their difference (t_c-t_p), Droplet solidification time (t_s), and Intrinsic contact angle of droplet at pinning (θ_{ip}). All the data are obtained for a constant $C_{NaCl} = 0.5$ (M).

C_{CTAB} (M)	$\theta_{Eqm.}(\circ)$	t_p (min)	t_c (min)	t_s (min)	t_c-t_p (min)	θ_{ip} (°)
0.0001	50	11.44	16	10.1	4.56	13.45
0.001	51.7	10.38	17.13	14.6	6.75	18
0.01	44	4.4	18.93	16.53	14.53	26.38
0.02	37	1.32	20.01	18.1	18.69	30
0.1	34	0.6	27.17	23.5	26.57	34

Table S5

C_{NaCl} (M)	0.5	0.5	0.5	0.5	0.5
C_{CTAB}	0.1	0.02	0.01	0.001	0.0001
m	1.2	1.04	1.02	1.002	1.0002
x_1	0.833	0.9615	0.9804	0.9980	0.9998
x_2	0.167	0.0385	0.0196	0.00199	0.000199

Table S6

Concentrations of CTAB (C_{CTAB} in (M)), Equilibrium contact angle, Droplet pinning time (t_p), Droplet crystallisation time (t_c), their difference (t_c-t_p), Droplet solidification time (t_s), and Intrinsic contact angle of droplet at pinning (θ_{ip}). All the data are obtained for a constant $C_{NaCl} = 2$ (M).

C_{CTAB} (M)	$\theta_{Eqm.}(\circ)$	t_p (min)	t_c (min)	t_s (min)	t_c-t_p (min)	θ_{ip} (°)
0.0001	50.6	27	27.73	30.07	0.73	15.26
0.001	49.2	16.02	22.24	29.56	6.04	16
0.01	49	7.22	18.6	25.07	11.38	26.9
0.02	47	4.56	17	24.37	12.44	29.7
0.1	32	0.3	12.9	6	12.6	32

Table S7

C_{NaCl} (M)	2	2	2	2	2
C_{CTAB}	0.1	0.02	0.01	0.001	0.0001
m	4.2	4.04	4.02	4.002	4.0002
x_1	0.952	0.9900	0.9950	0.9995	0.99995
x_2	0.0476	0.00990	0.00497	0.00049	0.000049

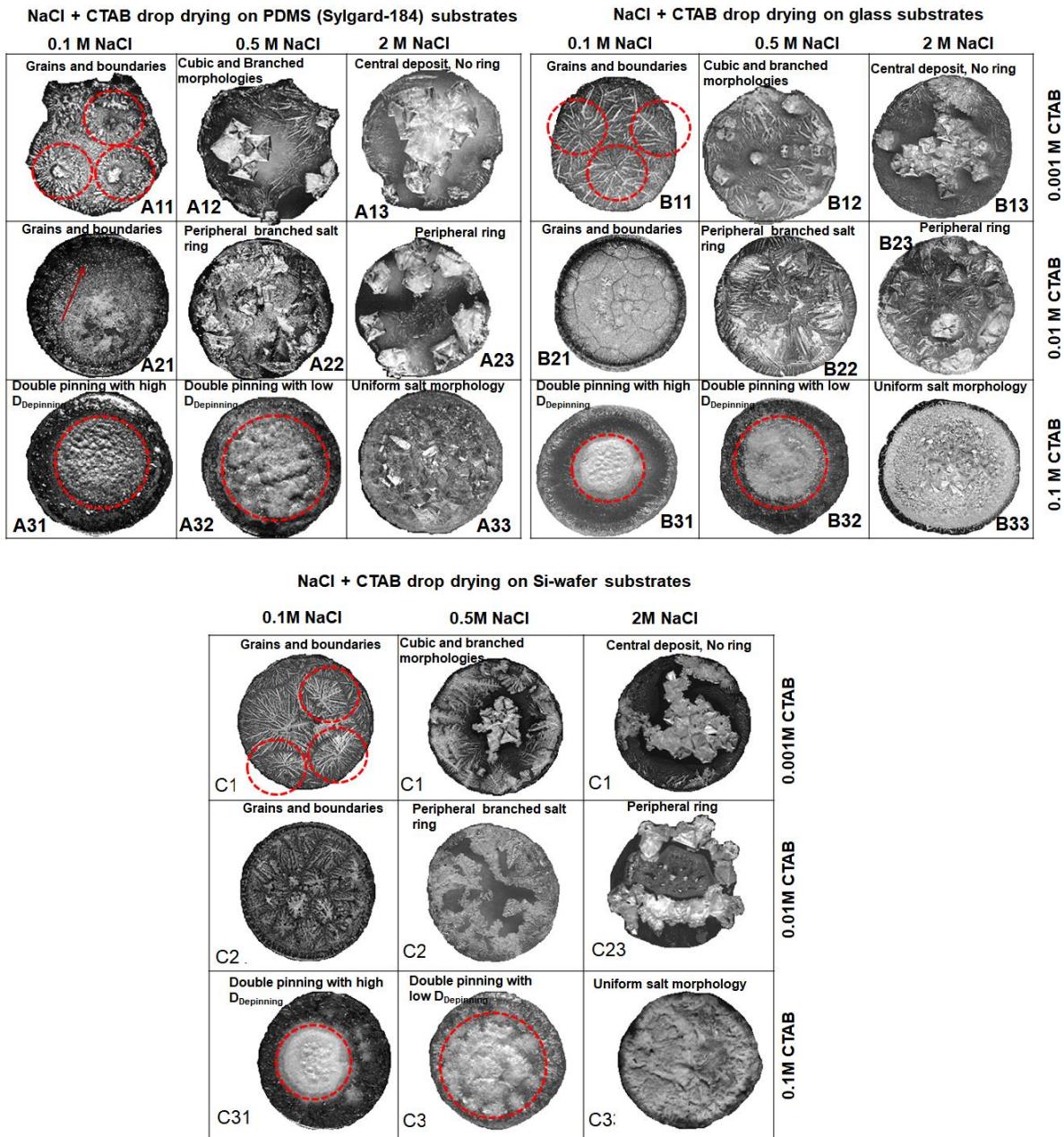


Figure S1: Evaporative drying of CTAB containing NaCl solution droplets on cross-linked PDMS Sylgard 184® substrates (A11 to A33), on glass substrates (B11 to B33), and on Si/SiO_x (100) wafer substrate (C11 to C33). Dried deposit diameter on the glass and Si/SiO_x (100) wafer substrates is ca. 2.6 mm, and the same on the cross-linked PDMS substrate is ca. 1.2 mm.

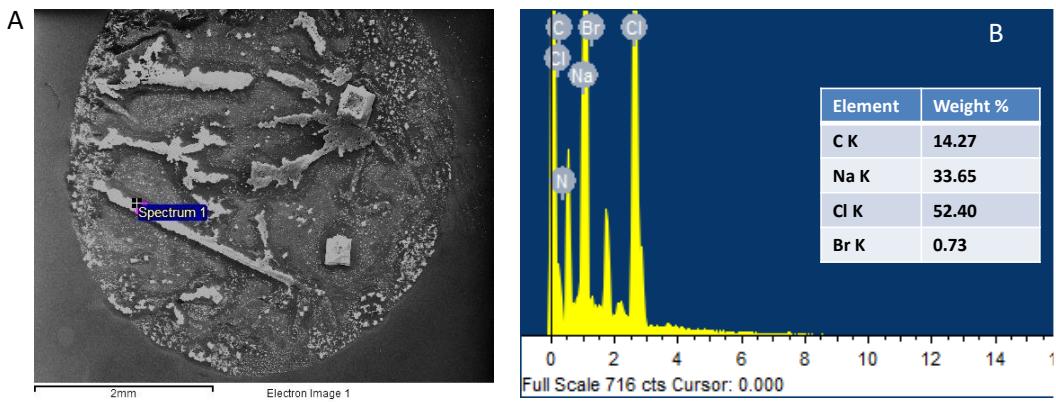


Figure S2: EDS measurement on the mm-long skeletal morphologies. It indicates that Na and Cl are the main components of such skeletal crystals.

List of supporting movies

#	Movie Particulars	Real total run time (s)
1	Movie 1: 0.1 M NaCl + 0.0001M CTAB	1376
2	Movie 2: 0.1 M NaCl + 0.001 M CTAB	1736
3	Movie 3: 0.1 M NaCl + 0.01 M CTAB	2232
4	Movie 4: 0.1 M NaCl + 0.1 M CTAB	4878
5	Movie 5: 0.5 M NaCl + 0.0001 M CTAB	1566
6	Movie 6: 0.5 M NaCl + 0.001 M CTAB	1904
7	Movie 7: 0.5 M NaCl + 0.01 M CTAB	2128
8	Movie 8: 0.5 M NaCl + 0.02 M CTAB	2287
9	Movie 9: 0.5 M NaCl + 0.1 M CTAB	3040
10	Movie 10: 2 M NaCl + 0.001 M CTAB	3108
11	Movie 11: 2 M NaCl + 0.01 M CTAB	2620
12	Movie 12: 2 M NaCl + 0.02 M CTAB	2482
13	Movie 13: 2 M NaCl + 0.1 M CTAB	1134