Electronic Supplementary Information

Influence of sol counter-ions on the anatase-to-rutile phase transformation and microstructure of nanocrystalline TiO_2

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Fig. S1 − Graphic output of the Rietveld refinement of the sample **HCL 450/4h**. The black open squares represent the observed pattern, the red line represent the calculated pattern, and the difference curve between observed and calculated profiles is plotted below. The position of reflections is indicated by the small vertical bars (black: anatase; red: rutile, orange brookite, and green: the internal standard used, NIST 676a).

Fig. S2 –XRPD patterns of the samples after being thermally treated at the 800 °C isotherm. a) **HNO_3**; b) **HCl**; c) **HBr** as sources of counter-ions. The vertical bars represent the XRPD peaks of rutile (red, JCPDS-PDF card no. 21-1276).

Fig. S3 − WPPM graphical output of sample **HNO_3 600/4h**. The black open squares represent the observed pattern, the red line represent the calculated pattern, and the difference curve between observed and calculated profiles is plotted below. The line-brake on the *y*-axis is supposed to emphasise the goodness of the fitting.

Fig. S4 − Size distribution, as obtained from the WPPM modelling, of sample **HNO_3 600** at the different dwell time used. a) anatase; b) rutile. The inset shows a magnification in order to highlight the minimum crystalline domain diameter detected.

Fig. S5 − Size distribution, as obtained from the WPPM modelling, of sample **HCl 600** at the different dwell time used. a) anatase; b) rutile. The inset shows a magnification in order to highlight the minimum crystalline domain diameter detected.

Fig. S6 − Size distribution, as obtained from the WPPM modelling, of sample **HBr 600** at the different dwell time used. a) anatase; b) rutile. The inset shows a magnification in order to highlight the minimum crystalline domain diameter detected.

Fig. S7 – Rutile size distribution at the different dwell time used, as obtained from the WPPM modelling, of samples: a) **HNO_3 800**; b) **HCl 800**; c) **HBr 800**.

Fig. S1

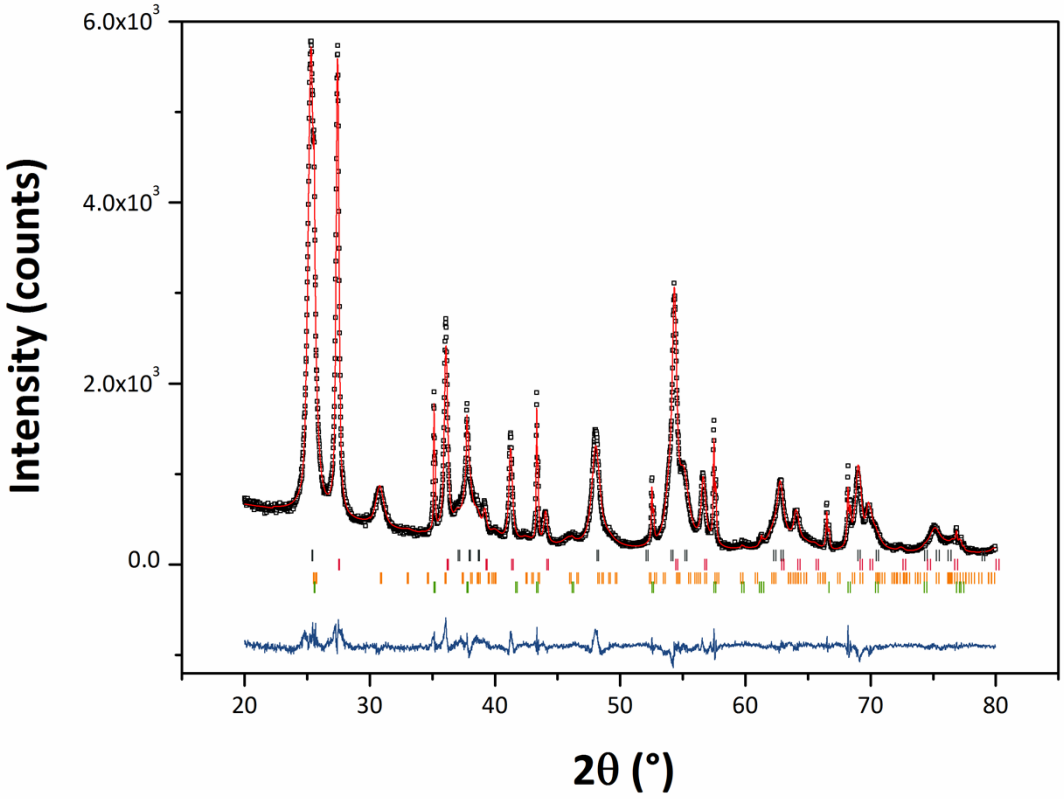

6.0x10^3
4.0x10^3
2.0x10^3
0.0
Intensity (counts)
20
30
40
50
60
70
80
2θ (°)

Fig. S2a

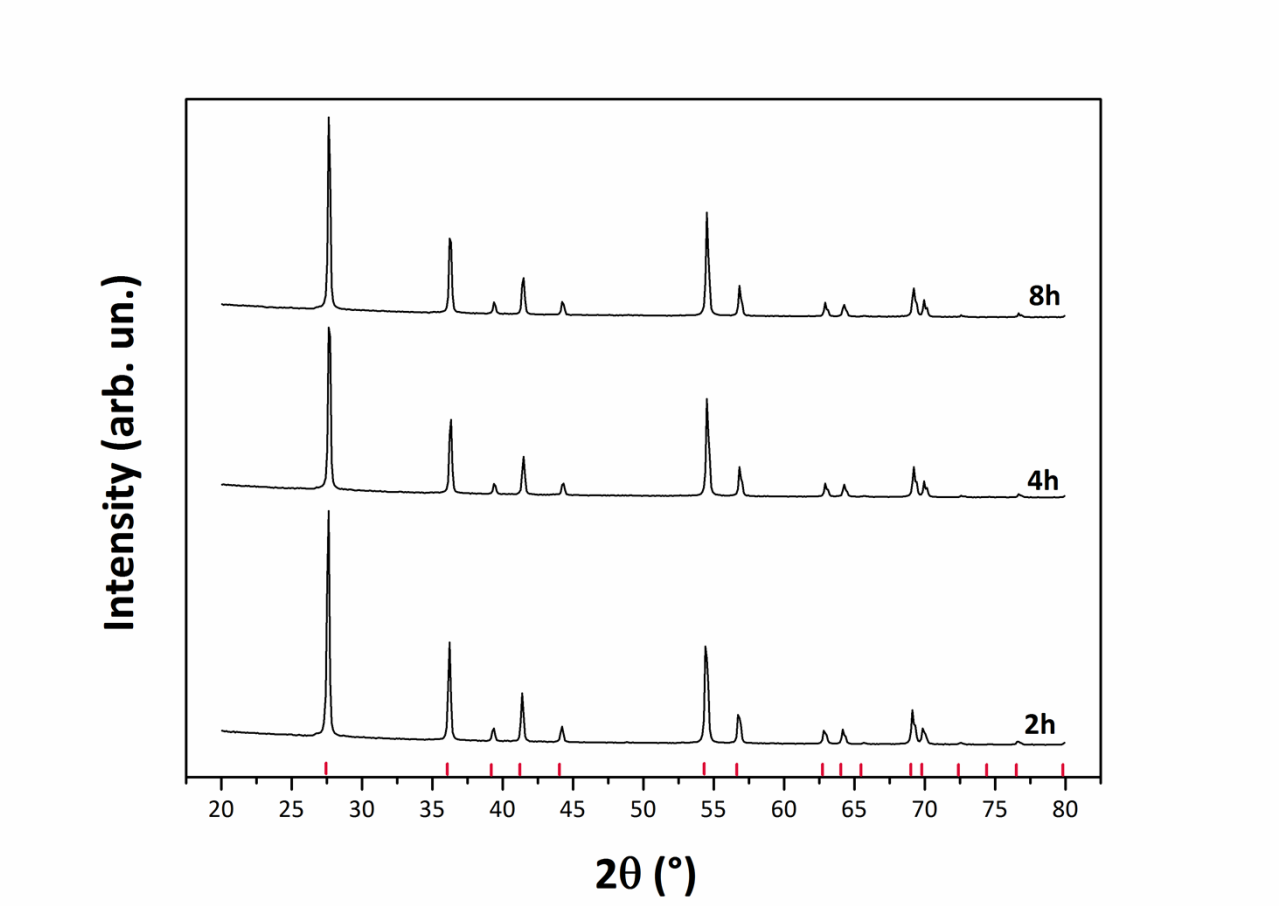


Fig. S2b

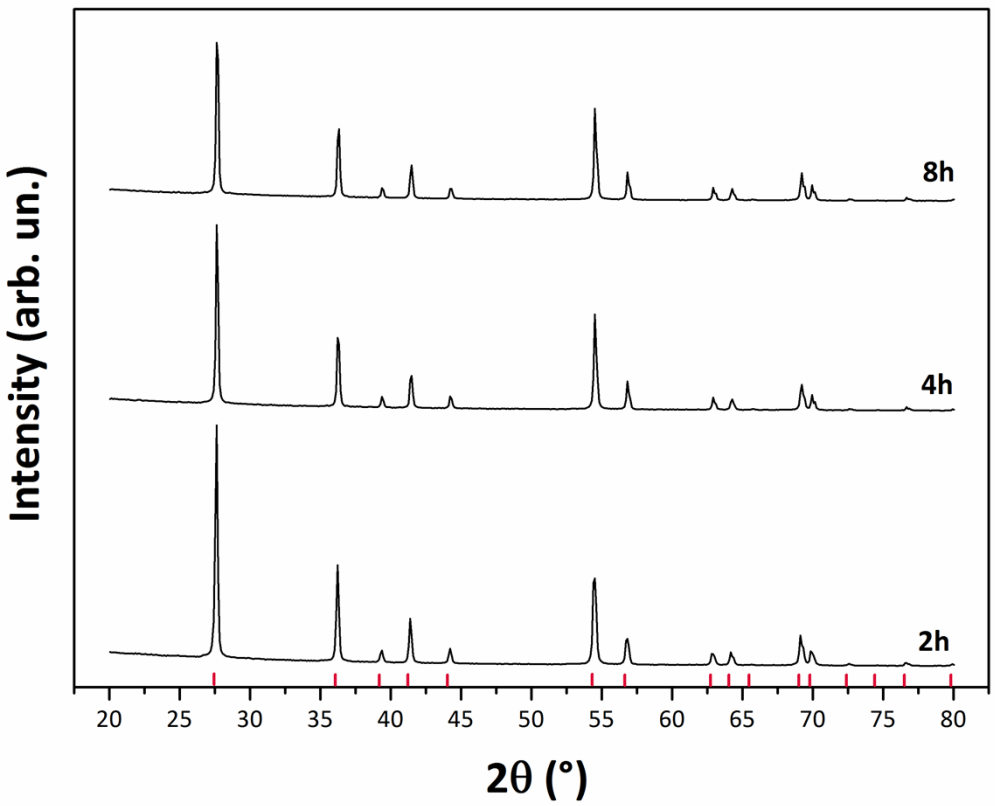


Fig. S2c

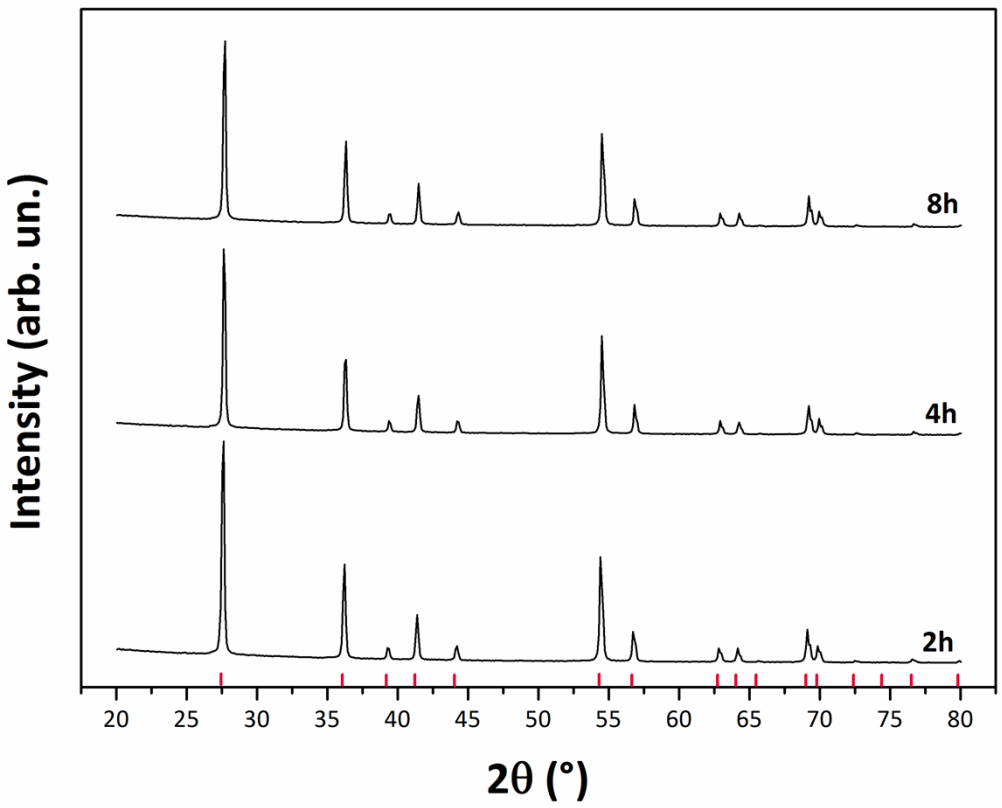
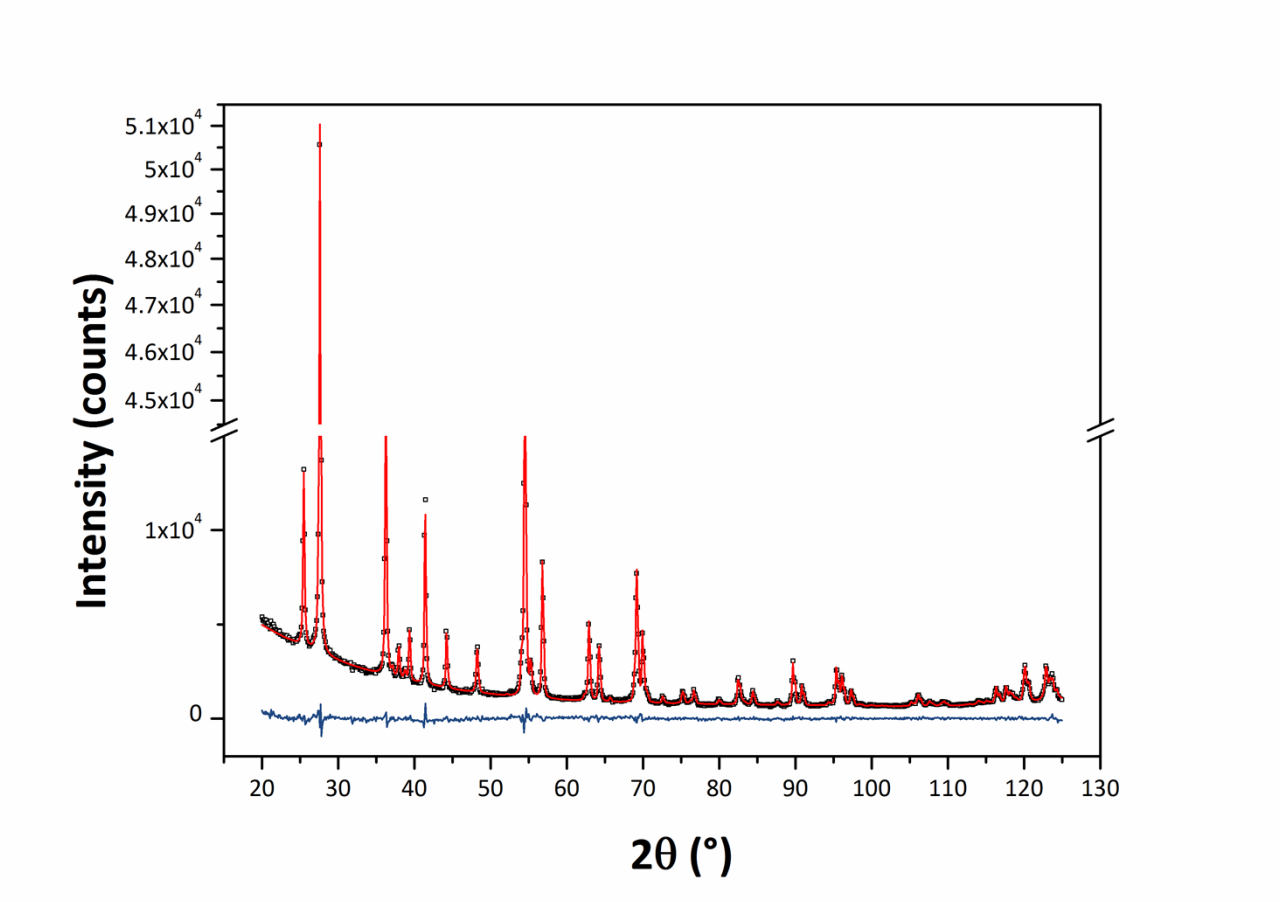


Fig. S3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5x10^4
4.9x10^4
4.8x10^4
4.7x10^4
4.6x10^4
4.5x10^4
1x10^4
0
20
30
40
50
60
70
80
90
100
110
120
130
2θ (°)

Fig. S4a

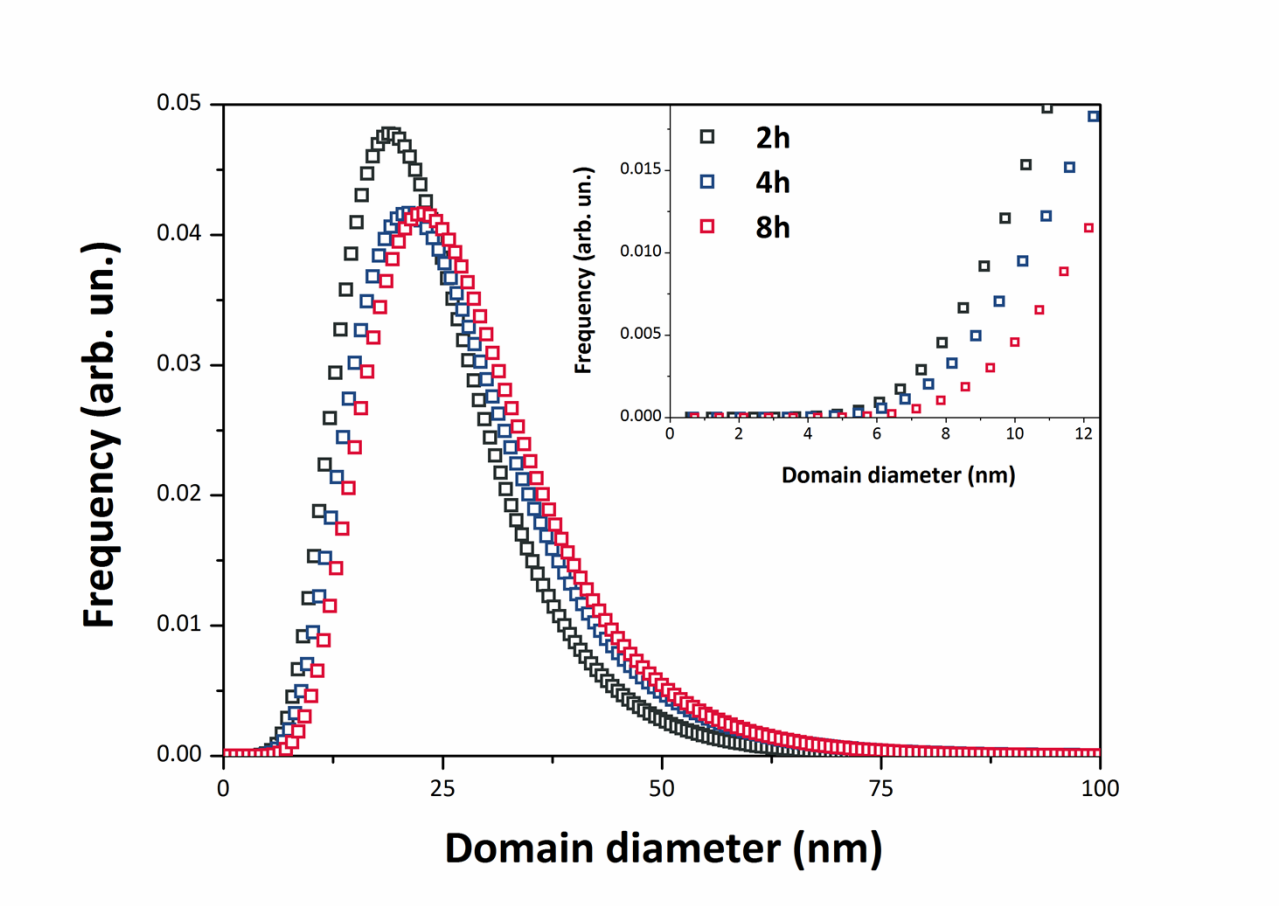
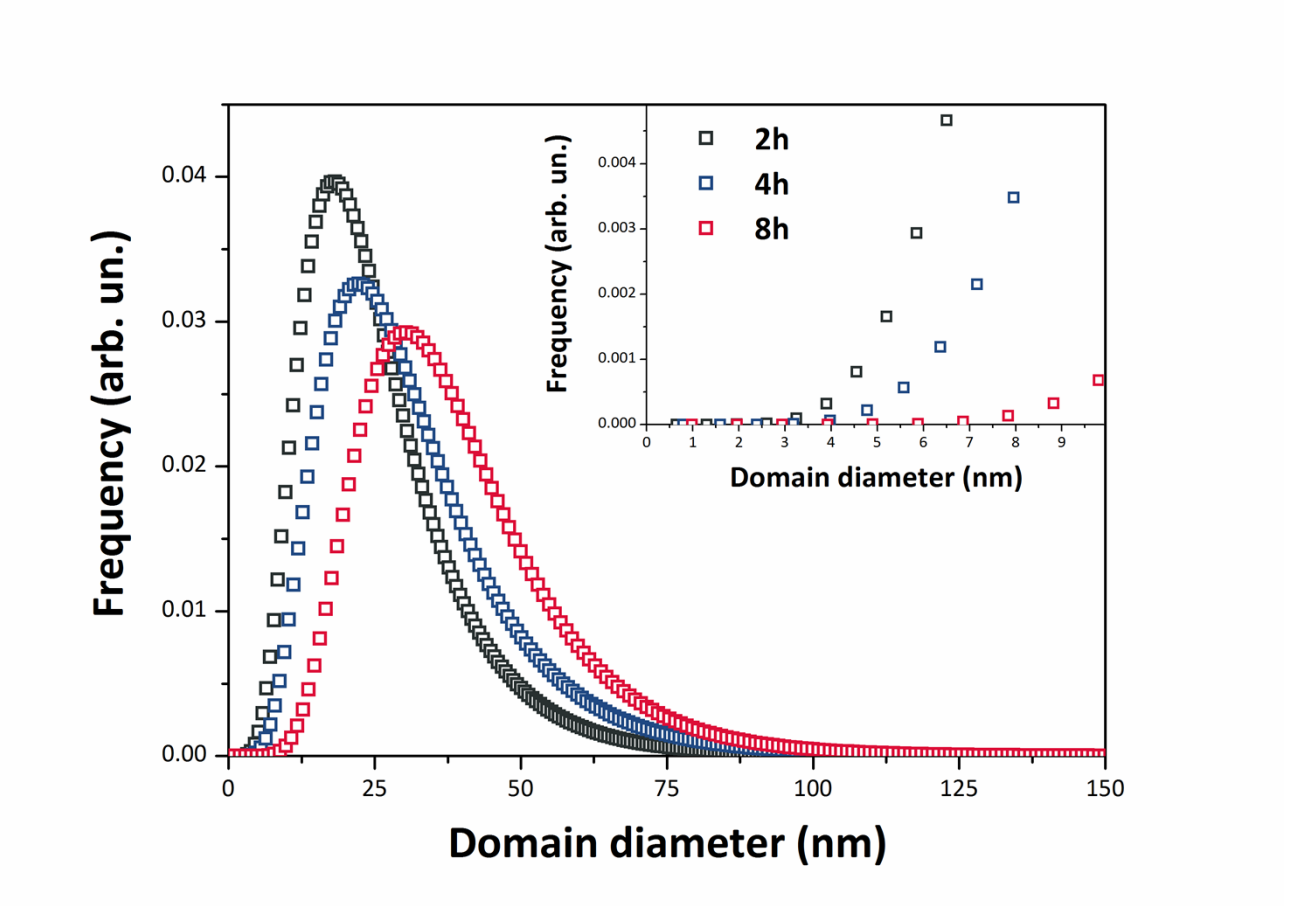

Frequency (arb. un.)
Domain diameter (nm)
0.00
0.01
0.02
0.03
0.04
0.05
0
25
50
75
100
2h
4h
8h
Frequency (arb. un.)
Domain diameter (nm)
0.000
0.005
0.010
0.015
0
2
4
6
8
10
12

Fig. S4b


Frequency (arb. un.)
Domain diameter (nm)
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0.01
0.02
0.03
0.04
0
25
50
75
100
125
150
2h
4h
8h
Frequency (arb. un.)
Domain diameter (nm)
0.000
0.001
0.002
0.003
0.004
0
1
2
3
4
5
6
7
8
9

Fig. S5a

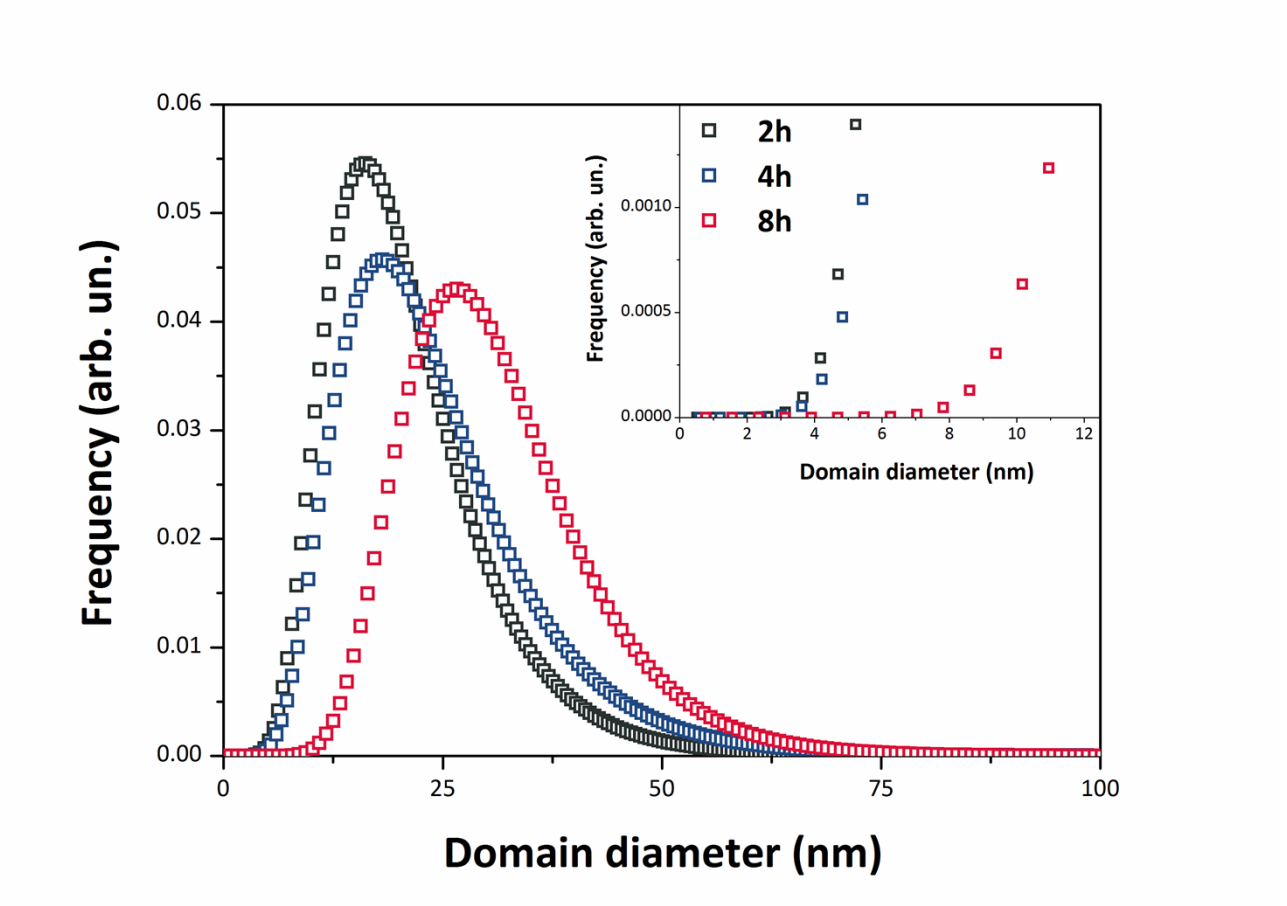

Frequency (arb. un.)
Domain diameter (nm)
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0
25
50
75
100
2h
4h
8h
Frequency (arb. un.)
0.0000
0.0005
0.0010
0
2
4
6
8
10
12
Domain diameter (nm)

Fig. S5b

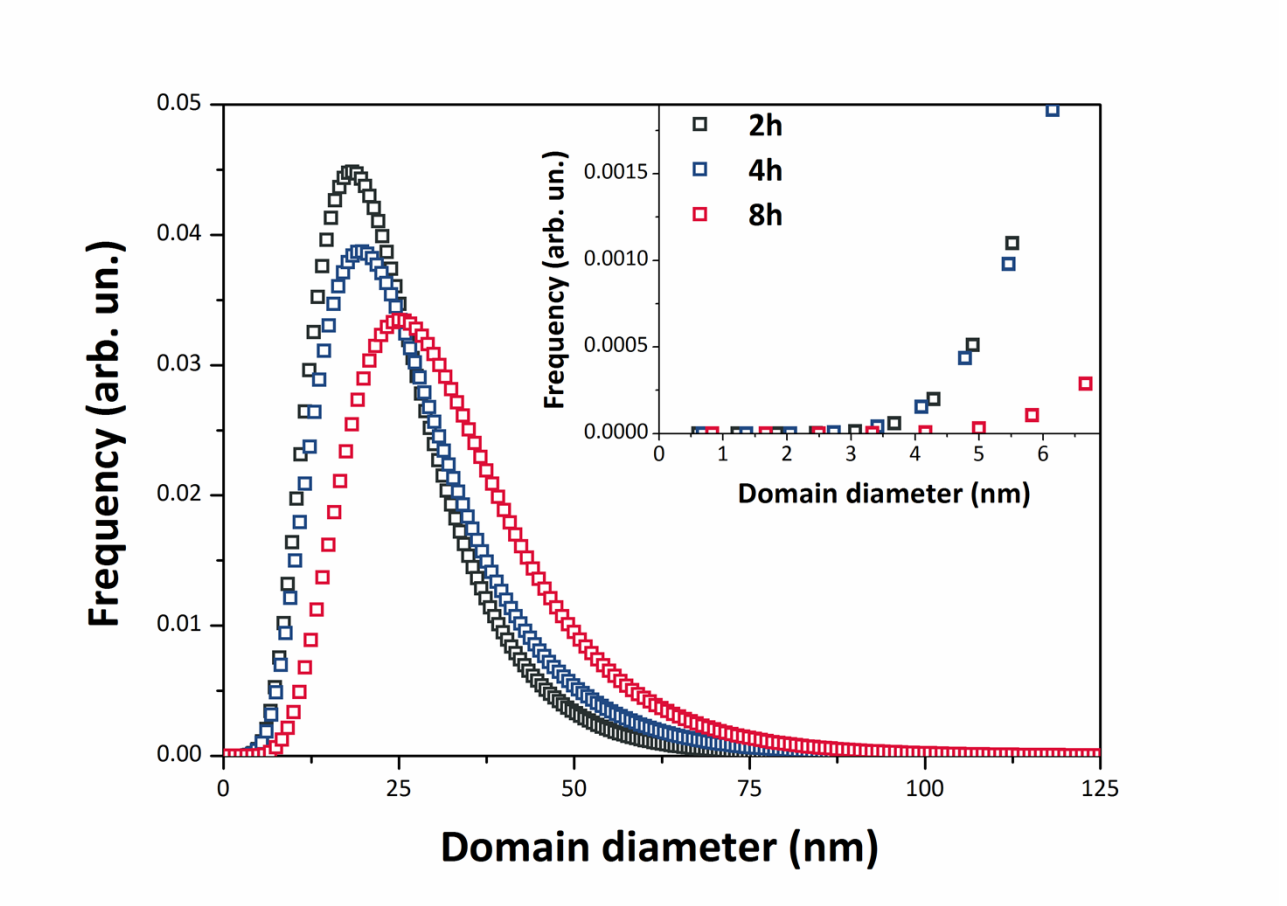

Frequency (arb. un.)
Domain diameter (nm)
0.05
0.04
0.03
0.02
0.01
0.00
0
25
50
75
100
125
2h
4h
8h
Frequency (arb. un.)
0.0015
0.0010
0.0005
0.0000
0
1
2
3
4
5
6
Domain diameter (nm)

Fig. S6a

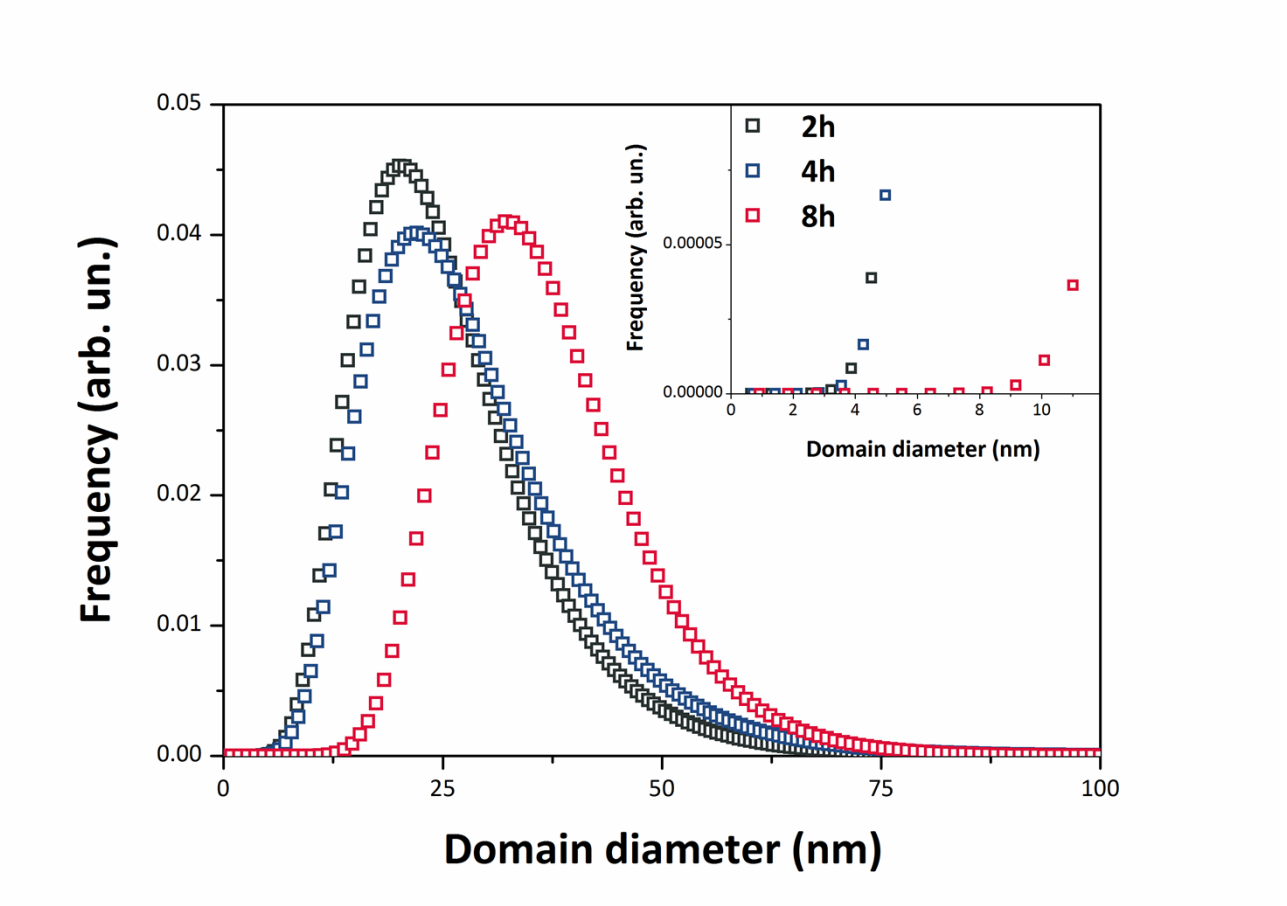

Frequency (arb. un.)
Domain diameter (nm)
0.05
0.04
0.03
0.02
0.01
0.00
0
25
50
75
100
2h
4h
8h
Frequency (arb. un.)
0.00005
0.00000
0
2
4
6
8
10
Domain diameter (nm)

Fig. S6b

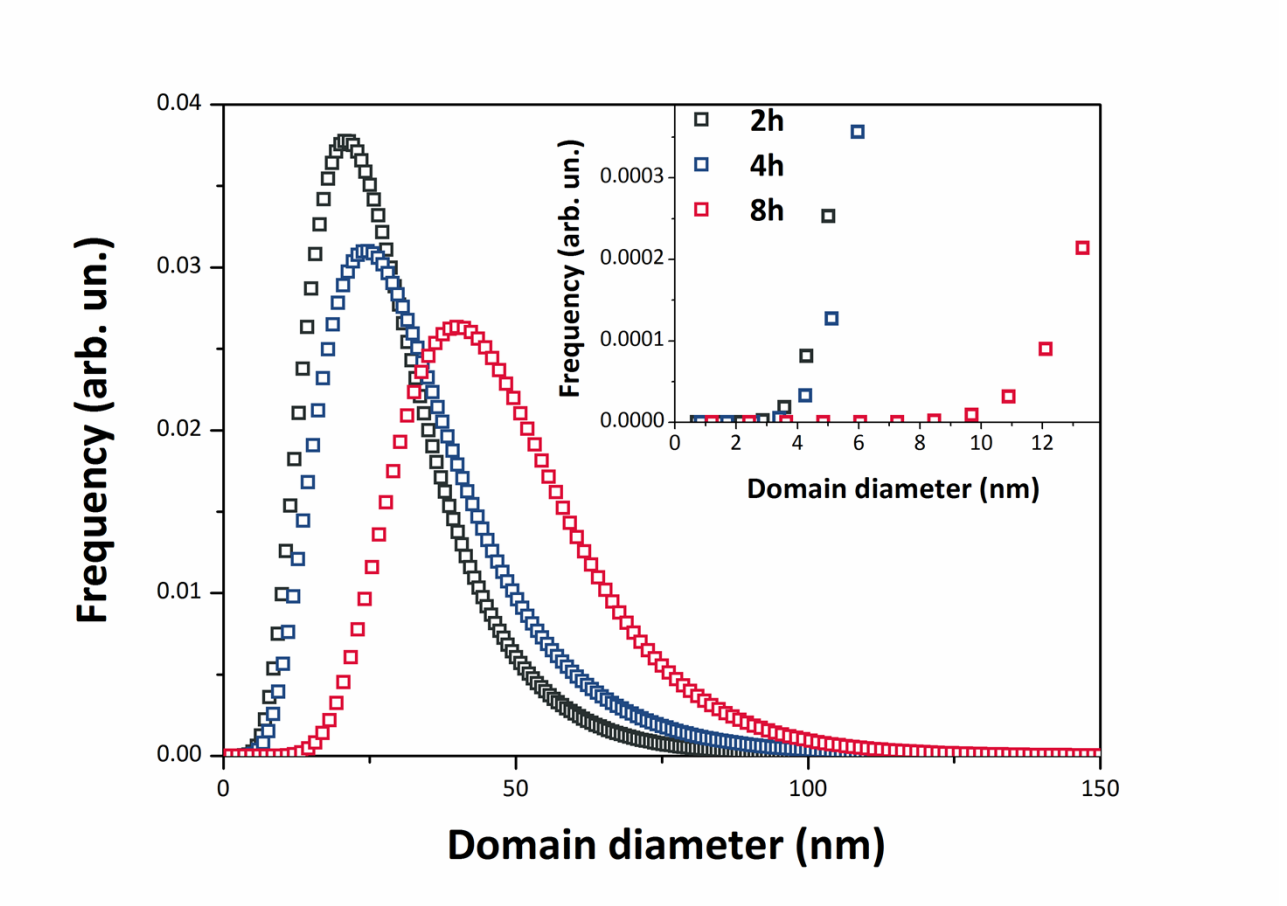

Frequency (arb. un.)
Domain diameter (nm)
0.00
0.01
0.02
0.03
0.04
0
50
100
150
2h
4h
8h
Frequency (arb. un.)
Domain diameter (nm)
0.0000
0.0001
0.0002
0.0003
0
2
4
6
8
10
12

Fig. S7a

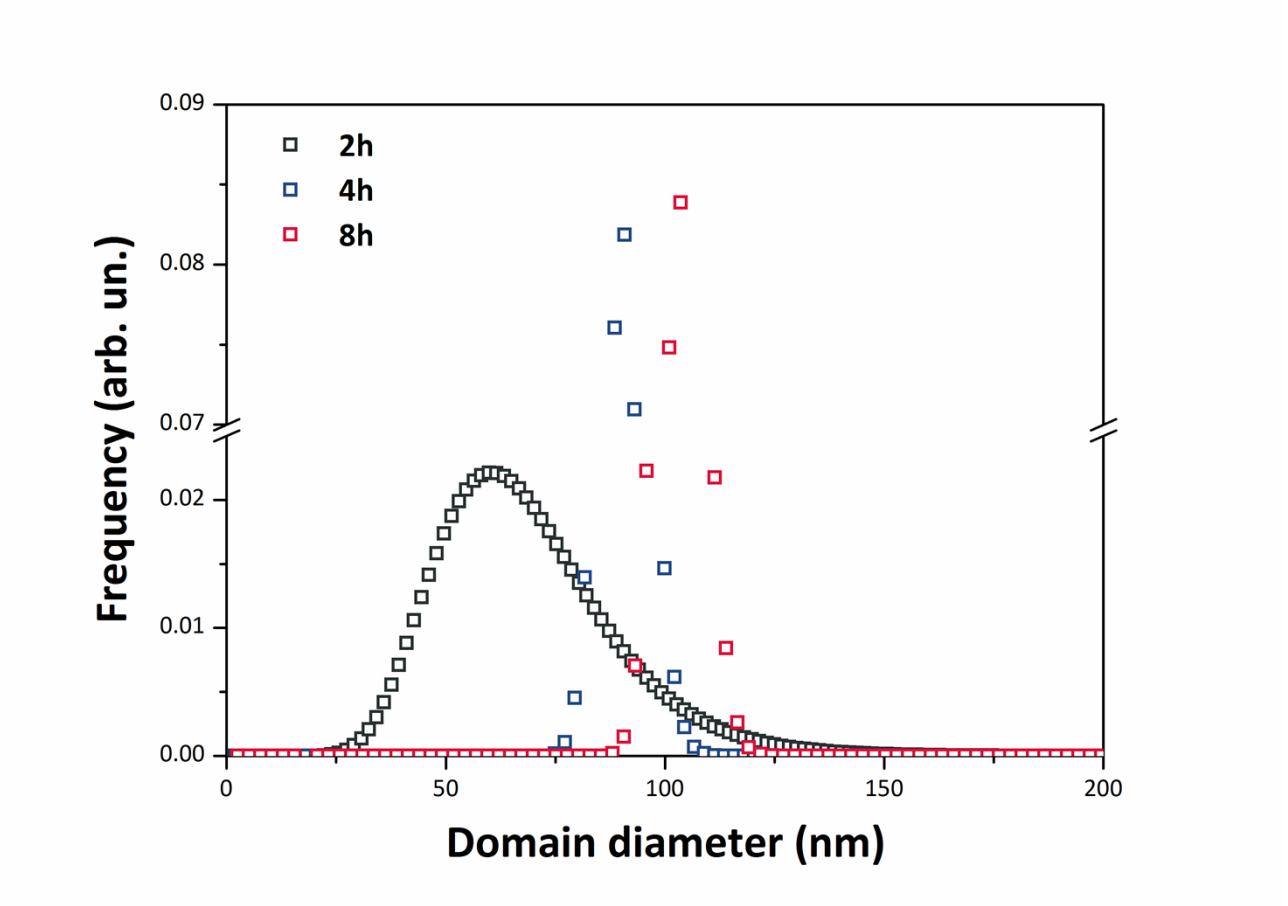

0.09
0.08
0.07
0.02
0.01
0.00
2h
4h
8h
Frequency (arb. un.)
0
50
100
150
200
Domain diameter (nm)

Fig. S7b

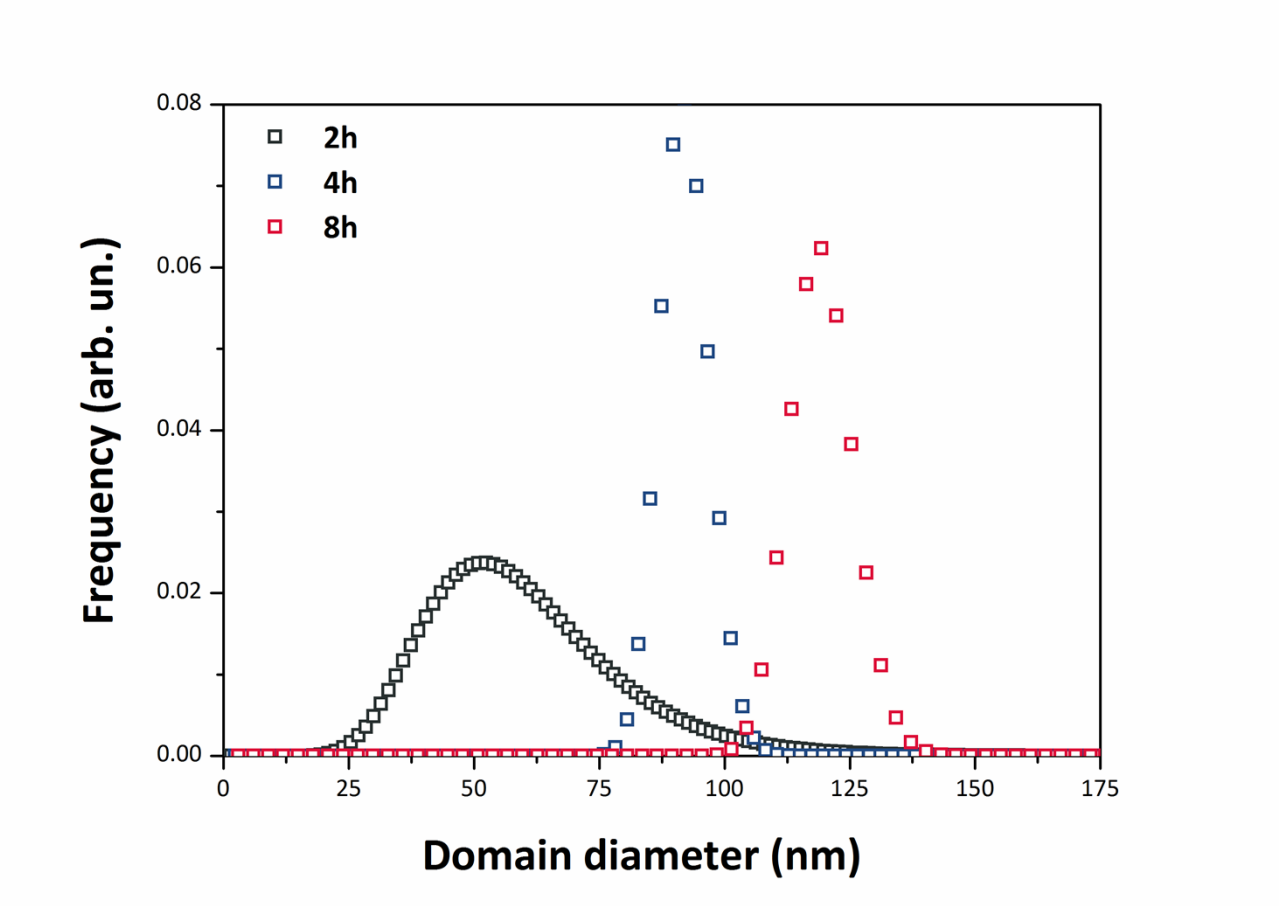
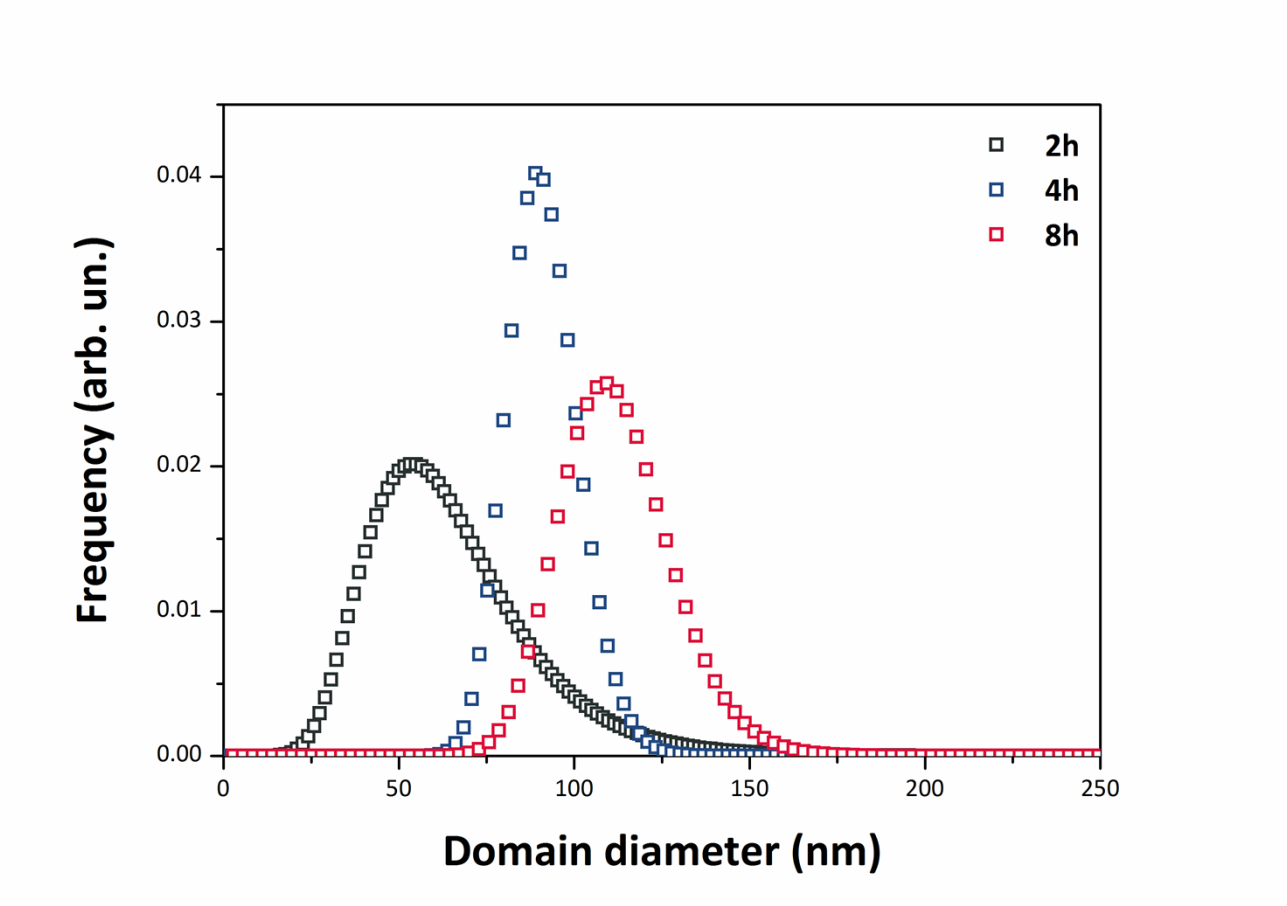

2h
4h
8h
Frequency (arb. un.)
0.08
0.06
0.04
0.02
0.00
0
25
50
75
100
125
150
175
Domain diameter (nm)

Fig. S7c


2h
4h
8h
Frequency (arb. un.)
0.04
0.03
0.02
0.01
0.00
0
50
100
150
200
250
Domain diameter (nm)