Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Evaporation-Induced Self-Structuring of Silica Nanohybrid Films during Spin-Coating: Structural Evolution via Cooperative Physical and Chemical Interactions

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SUPPORTING INFORMATION

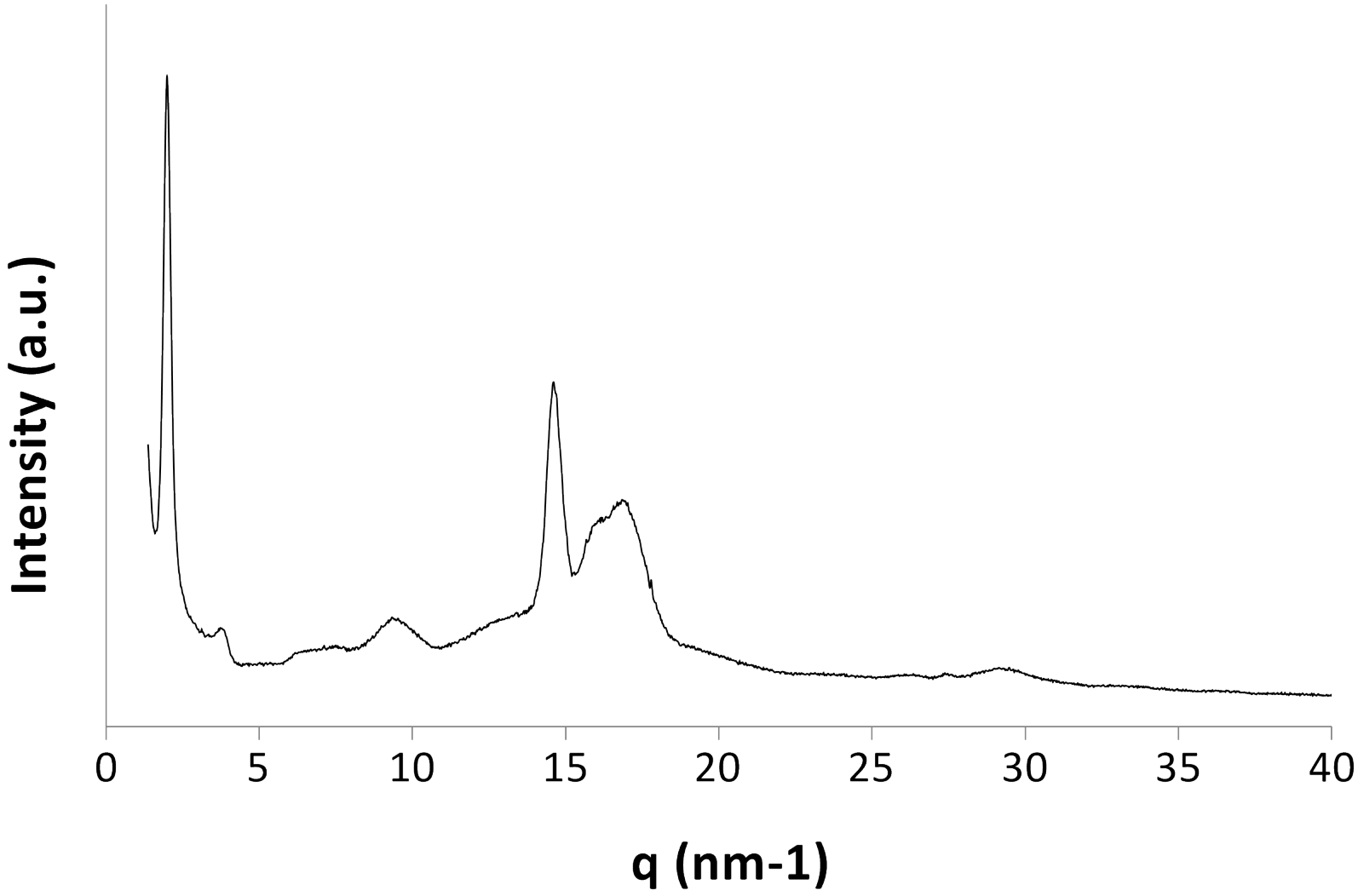
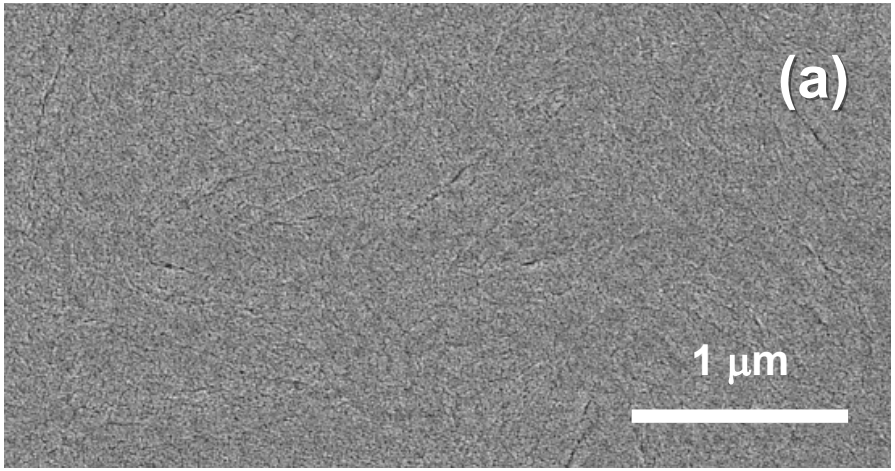
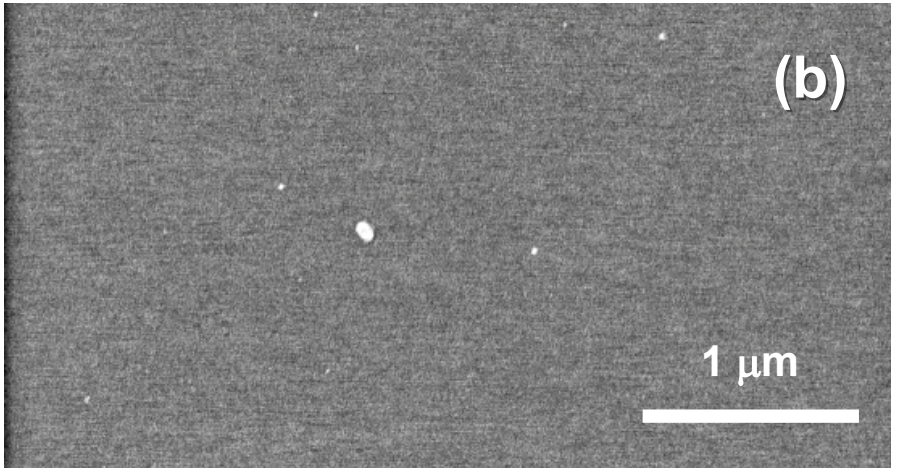


Figure S1. X-ray powder diffraction pattern of the powder obtained from **P12** in 1-propanol under HCl-catalysed conditions (mole ratio **P12**:HCl:H_2O:1-PrOH, 1:0.0054:45:1152, 3 days aging time)





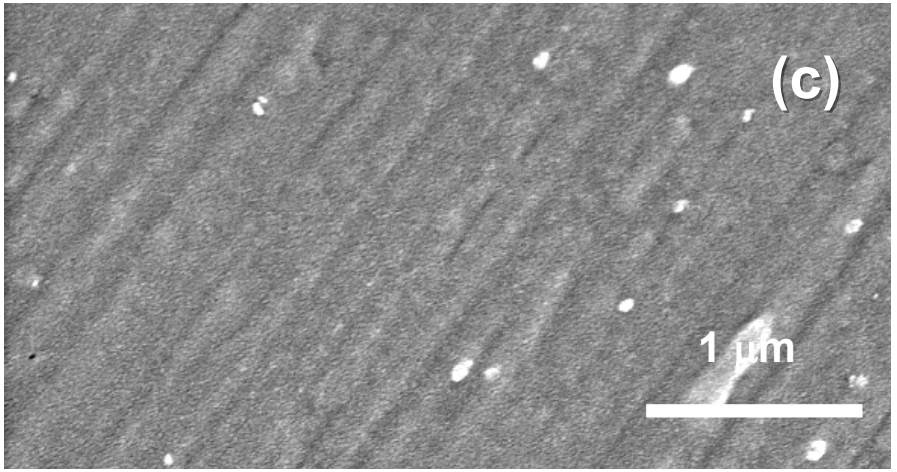


Figure S2. SEM micrographs of coatings produced under (a) HCl-; (b) NH_4F-; and (c) NH_4OH-catalysed conditions (Size bar, 1 μm. Coating parameters: 1 % P12 in 1-PrOH; Si:H_2O = 1:23; ageing time = 4 h; spinning speed=8000 min^{-1} for 60 s).

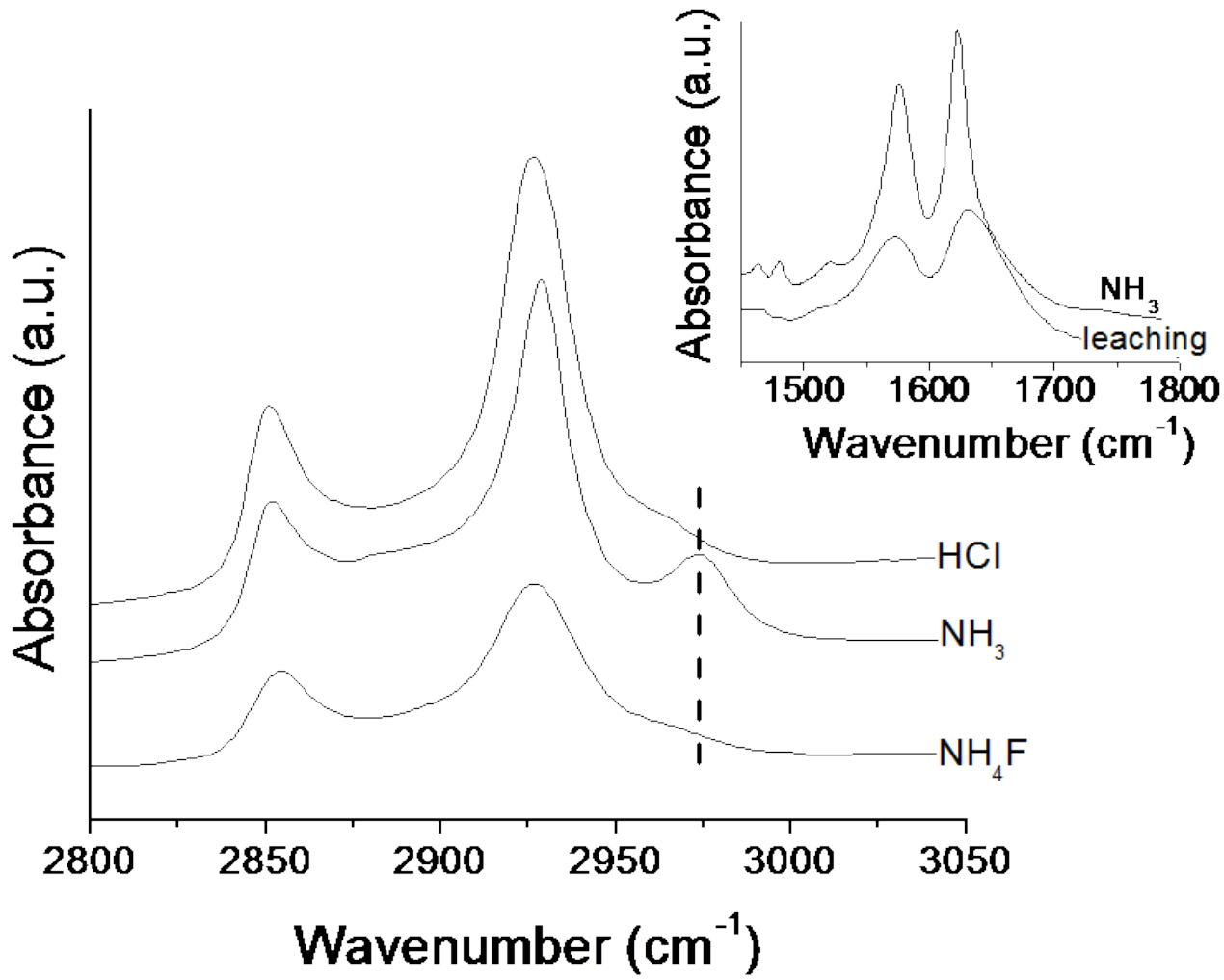


Figure S3. Infrared spectra of films produced from sols prepared using HCl, NH_3 or NH_4F as catalyst (Conditions: 1 % **P12** in 1-PrOH; Si:H_2O = 1:23; ageing time = 4 h; spinning speed=8000 min^{-1} for 60 s). The peak marked with a dashed line at 2974 cm^{-1} arises from unreacted **P12**. Inset: variations in the amide 1/2 region for the coating prepared from an NH_3-catalysed sol, before and after leaching in refluxing EtOH.

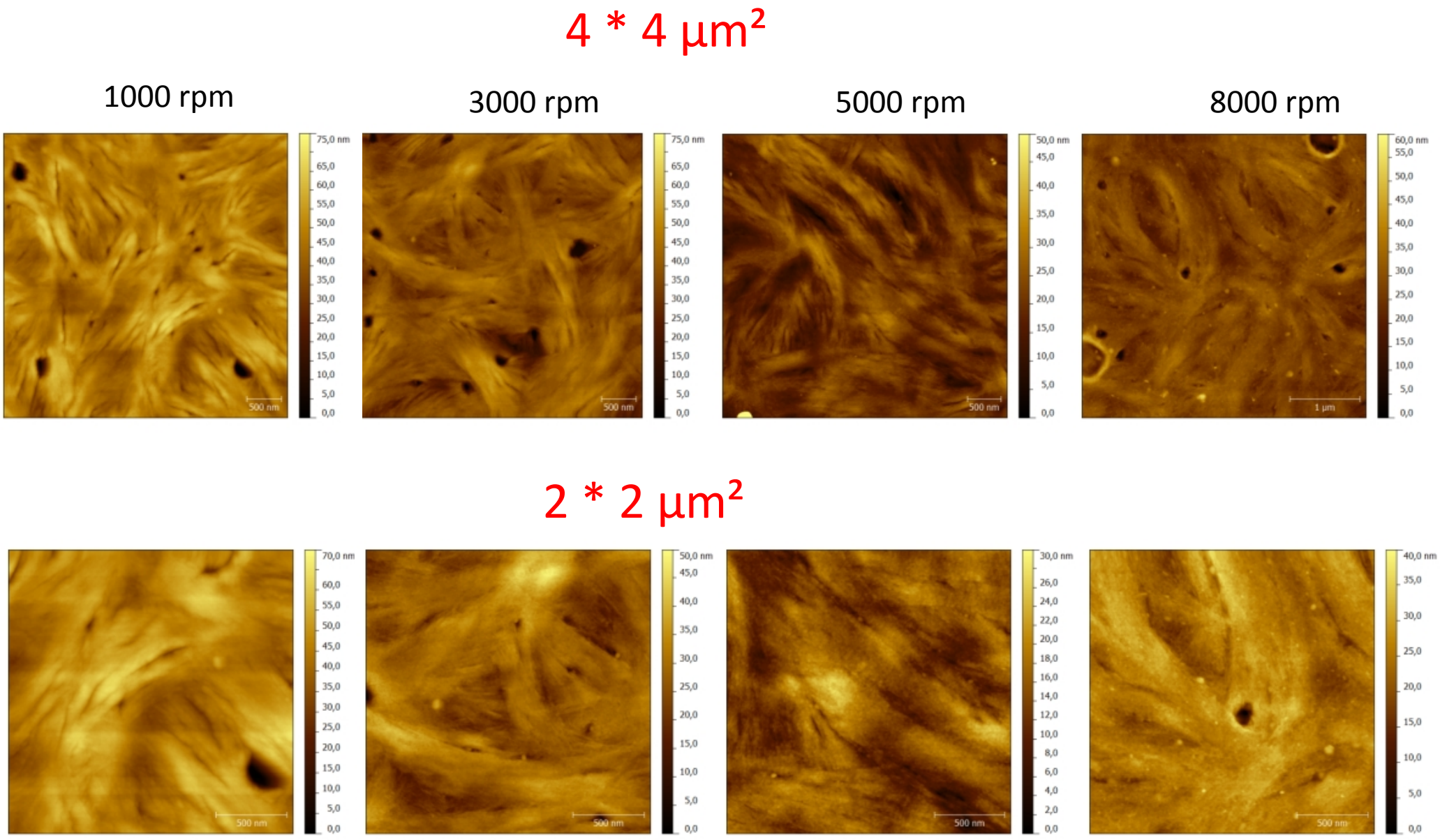


Figure S4. High-resolution AFM micrographs of coatings produced under HCl-catalysed conditions (Coating conditions: 1 % P12 in 1-PrOH; Si:H_2O = 1:23; ageing time = 4 h at varied spinning speed for 60 s).

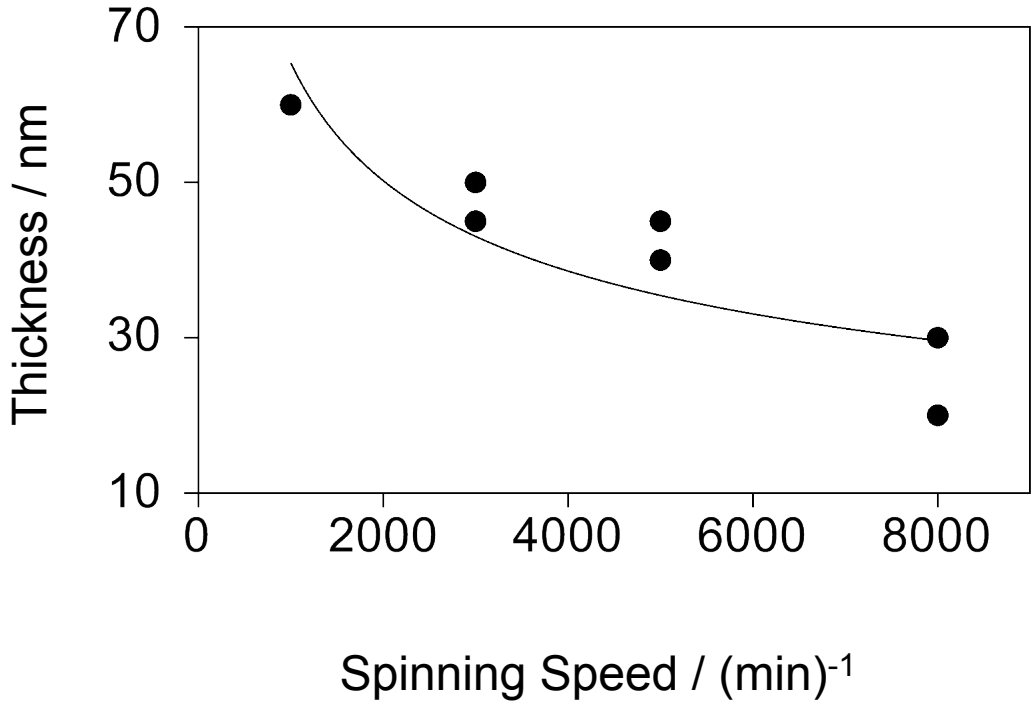


Figure S5. Thickness of coatings deposited from HCl-catalysed sols as a function of spinning speed (Coating parameters: 1 % **P12** in 1-PrOH; Si:H_2O = 1:23; ageing time = 4 h; spinning duration=60 s).

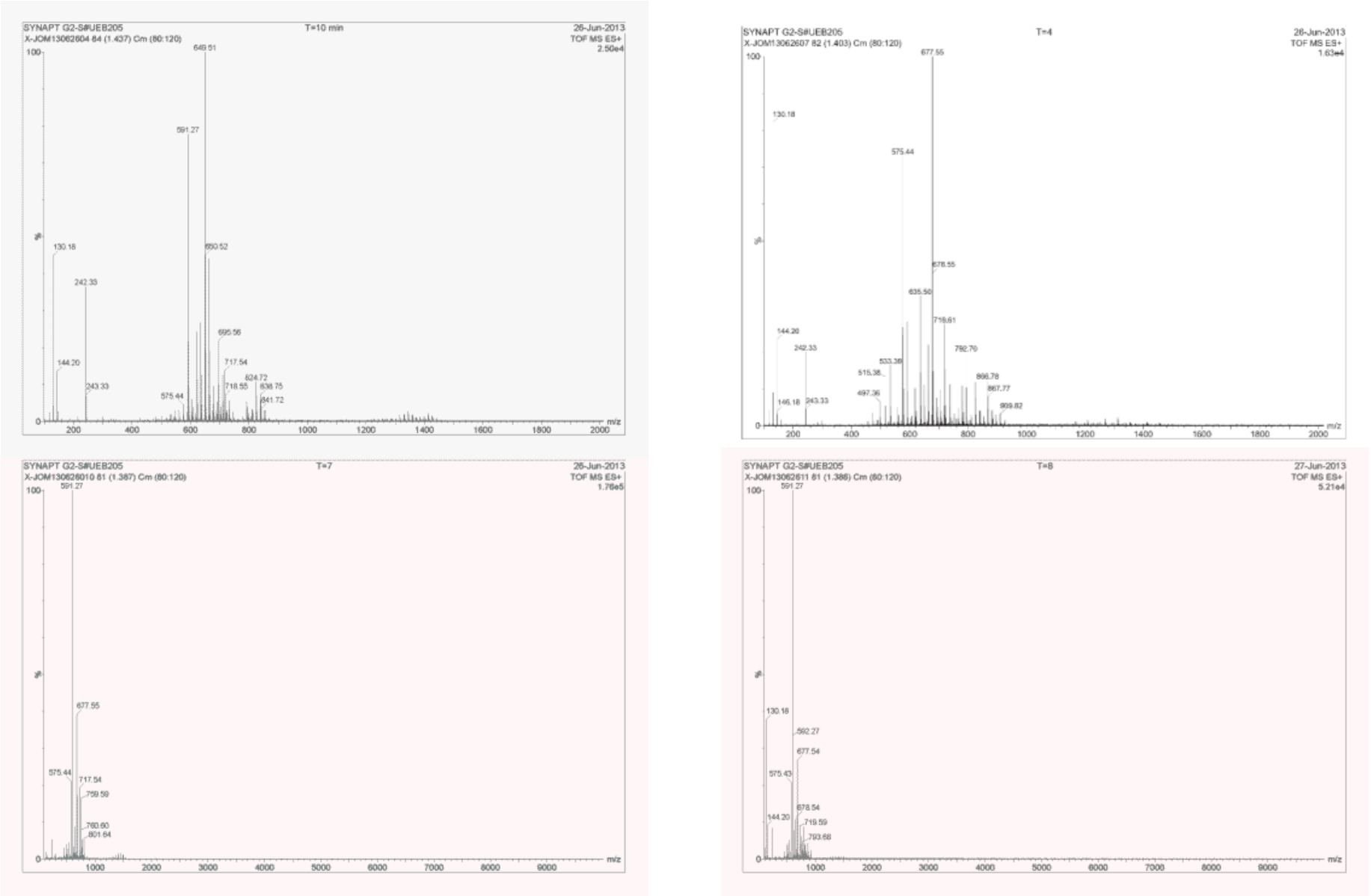
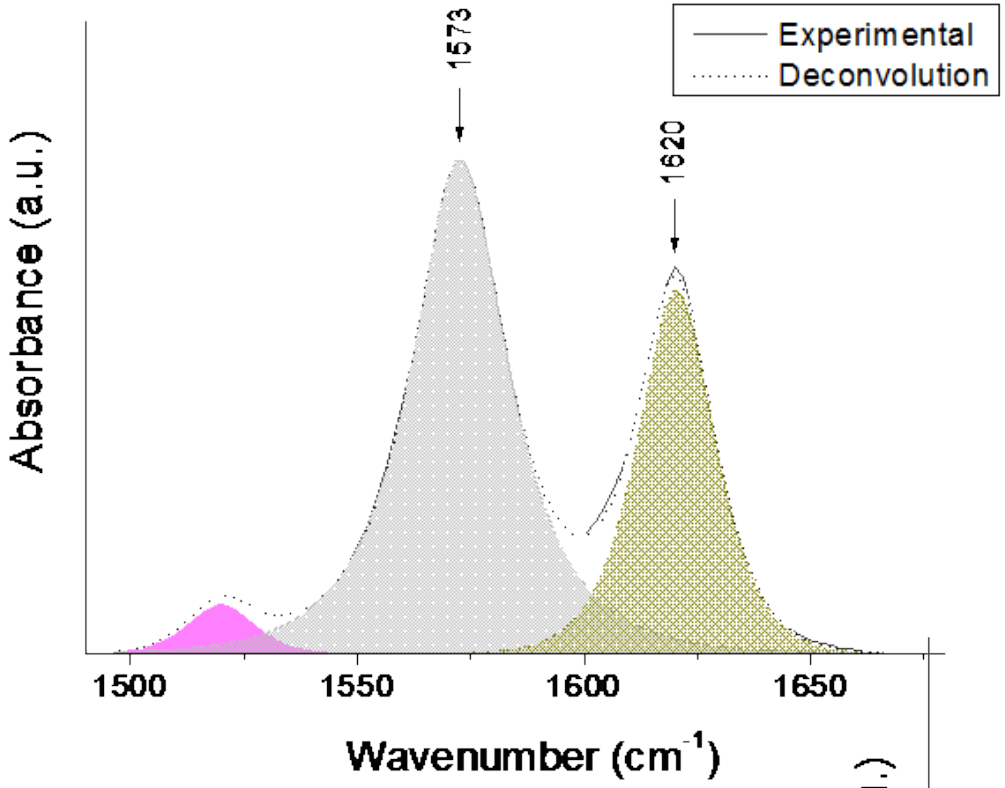


Figure S6. Variations in the mass spectra obtained from HCl-catalysed sols as a function of ageing time (10 minutes; 46 minutes; 4 hours and 24 hours).



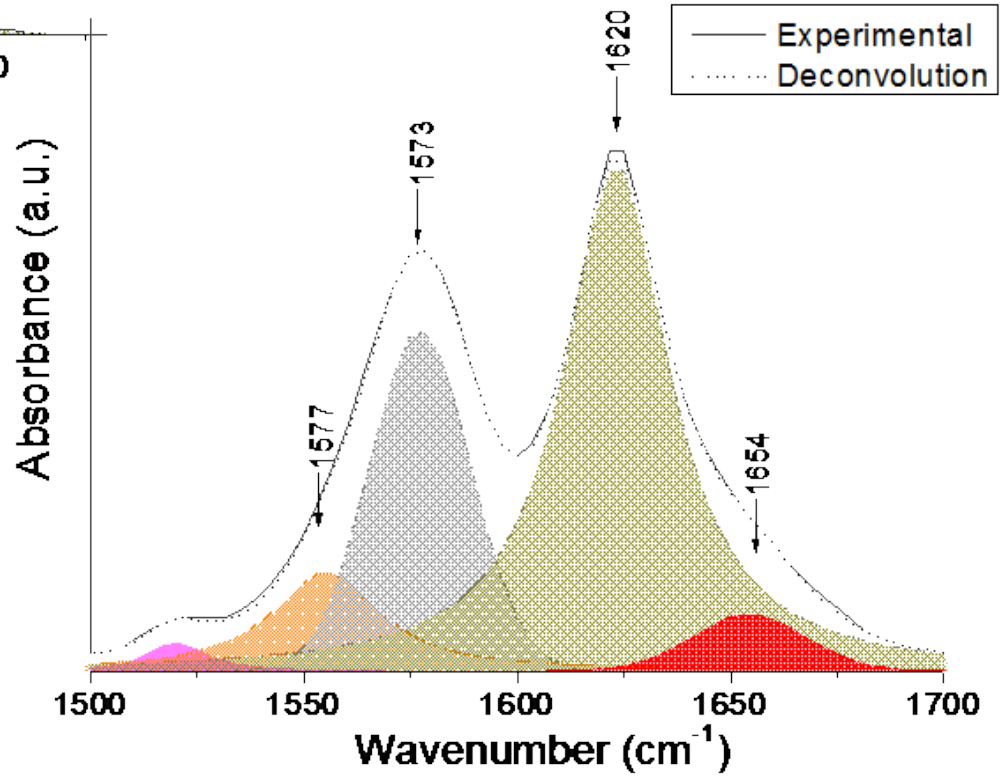


Figure S7. Curve fitting infrared spectra of **P12** (top) and coatings deposited from HCl-catalysed sol (bottom) (Conditions for depositing coating: 1 % **P12** in 1-PrOH; Si:H_2O = 1:23; ageing time = 4 h; spinning speed=8000 min^{-1} for 60 s).

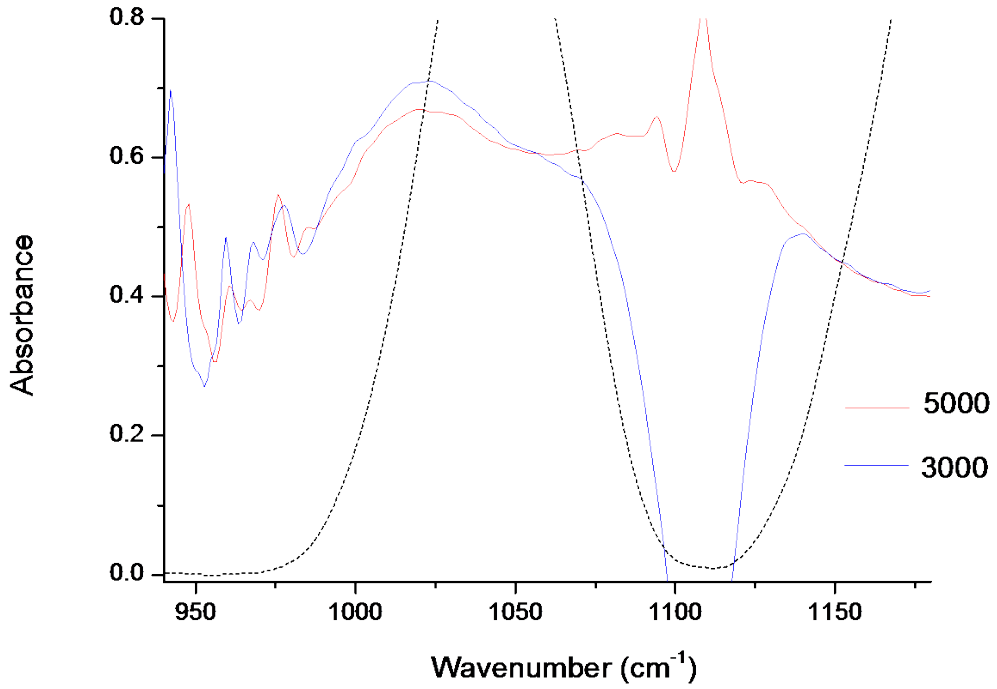


Figure S8. Infrared spectra in the region of SiOSi vibrations of coatings deposited from HCl-catalysed sols as a function of spinning speed. (Conditions for depositing coating: 1 % **P12** in 1-PrOH; Si:H_2O = 1:23; ageing time = 4 h; spinning speed=3000 and 5000 min^{-1} for 60 s). Dashed curve represents the exploitable infrared domain from 984 to 1072 cm^{-1} and above 1140 cm^{-1} (single beam for the wafer substrate).

Table S1. Band parameters obtained via curve fitting for **P12** and for coatings produced under HCl- and NH_4F-catalysed conditions

Sample[1]	ν/cm^{-1} (Relative Peak Area)				FWHM/cm^{-1}				$\Delta_{(2-3)}$ /cm^{-1}	$\Delta_{(1-4)}$ /cm^{-1}
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 1	Peak 2	Peak 3	Peak 4		
P12		1620 (35)	1573 (65)			20	25		47	
HCl-Cat	1654 (5)	1623 (57)	1577 (27)	1555 (11)	32	30	28	31	46	99
NH_4F-Cat	1662 (13)	1631 (41)	1573 (36)	1545 (10)	40	41	37	39	58	117

[1]HCl-Cat, film prepared from HCl-catalysed sol; NH_4F-Cat, film prepared from NH_4F-catalysed sol. Conditions: 1 % **P12** in 1-PrOH; Si:H_2O = 1:23; ageing time = 4 h; spinning speed = 8000 min^{-1} for 60 s

Table S2. Band parameters obtained via curve fitting for coatings produced under HCl-catalysed conditions, as a function of spinning speed

Spinning Speed[1]	ν/cm^{-1} (Relative Peak Area)				FWHM/cm^{-1}				$\Delta_{(2-3)}$ /cm^{-1}	$\Delta_{(1-4)}$ /cm^{-1}
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 1	Peak 2	Peak 3	Peak 4		
1000	1646 (21)	1624 (36)	1577 (24)	1555 (19)	49	28	31	37	47	91
3000	1648 (17)	1624 (39)	1577 (26)	1555 (18)	44	28	31	37	47	93
5000	1649 (14)	1625 (43)	1577 (26)	1555 (17)	41	30	31	37	48	94
8000	1649 (16)	1625 (46)	1577 (23)	1556 (15)	39	33	29	31	48	93

[1]Coating conditions: 1 % **P12** in 1-PrOH; Si:H_2O = 1:23; ageing time = 4 h; spinning time = 60 s

Table S3. Band parameters obtained via curve fitting for coatings produced under HCl-catalysed conditions, as a function of spinning speed

Spinning Speed and IR Beam Orientation[1,2]	ν/cm^{-1} (Relative Peak Area)				FWHM/cm^{-1}				I_2/I_1
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 1	Peak 2	Peak 3	Peak 4	
1000 (V)	1647 (35)	1624 (19)	1577 (30)	1558 (16)	52	24	33	43	0.54
1000 (H)	1649 (18)	1624 (28)	1577 (36)	1557 (18)	43	24	35	44	1.56
3000 (V)	1647 (33)	1624 (21)	1578 (26)	1559 (20)	52	26	31	46	0.64
3000 (H)	1649 (23)	1624 (27)	1576 (37)	1557 (13)	48	25	35	44	1.17
5000 (V)	1647 (32)	1624 (21)	1578 (30)	1557 (17)	52	26	32	41	0.66
5000 (H)	1649 (19)	1624 (29)	1577 (39)	1557 (13)	43	25	35	44	1.53
8000 (V)	1647 (37)	1625 (18)	1578 (28)	1558 (17)	52	26	32	43	0.49
8000 (H)	1650 (19)	1624 (29)	1577 (36)	1557 (16)	43	25	35	44	1.53

[1]Coating conditions: 1 % **P12** in 1-PrOH; Si:H_2O = 1:23; ageing time = 4 h; spinning time = 60 s

[2]IR radiation oriented horizontally (H) or vertically (V) with respect to the substrate

Table S4. Band parameters obtained via curve fitting for coatings produced under HCl-catalysed conditions, as a function of ageing time

Ageing Time (h)	ν/cm^{-1} (*Relative Peak Area*)				FWHM/cm^{-1}				I_2/I_1
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 1	Peak 2	Peak 3	Peak 4	
4	1654 (***5***)	1623 (***57***)	1577 (***27***)	1555 (***11***)	32	30	28	31	11.4
24	1650 (***11***)	1624 (***22***)	1579 (***53***)	1560 (***14***)	40	30	28	31	2