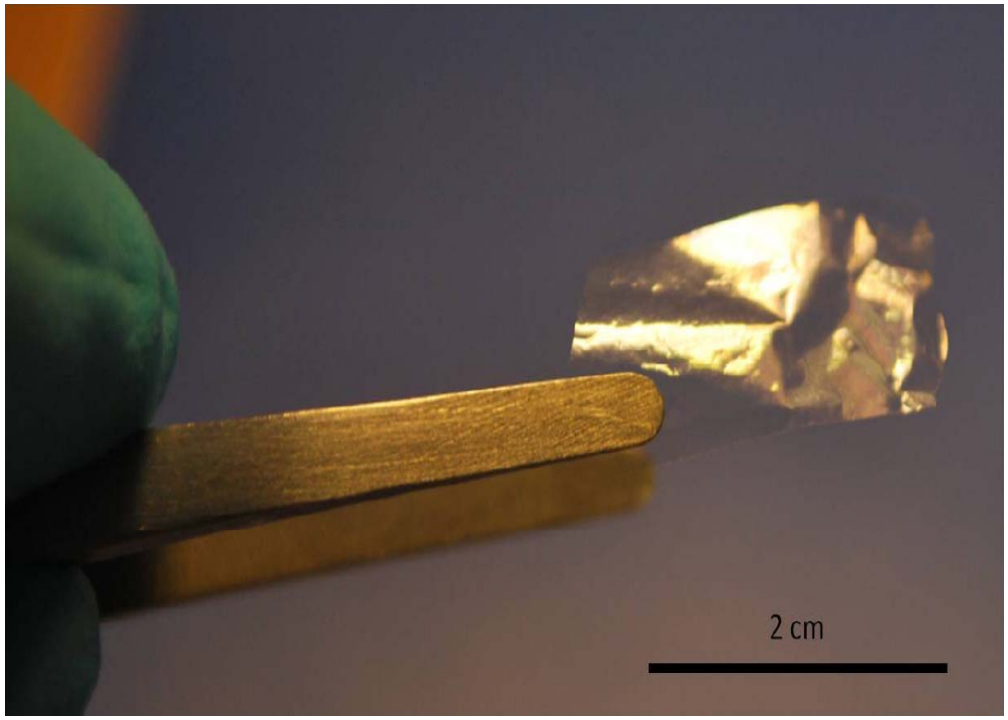
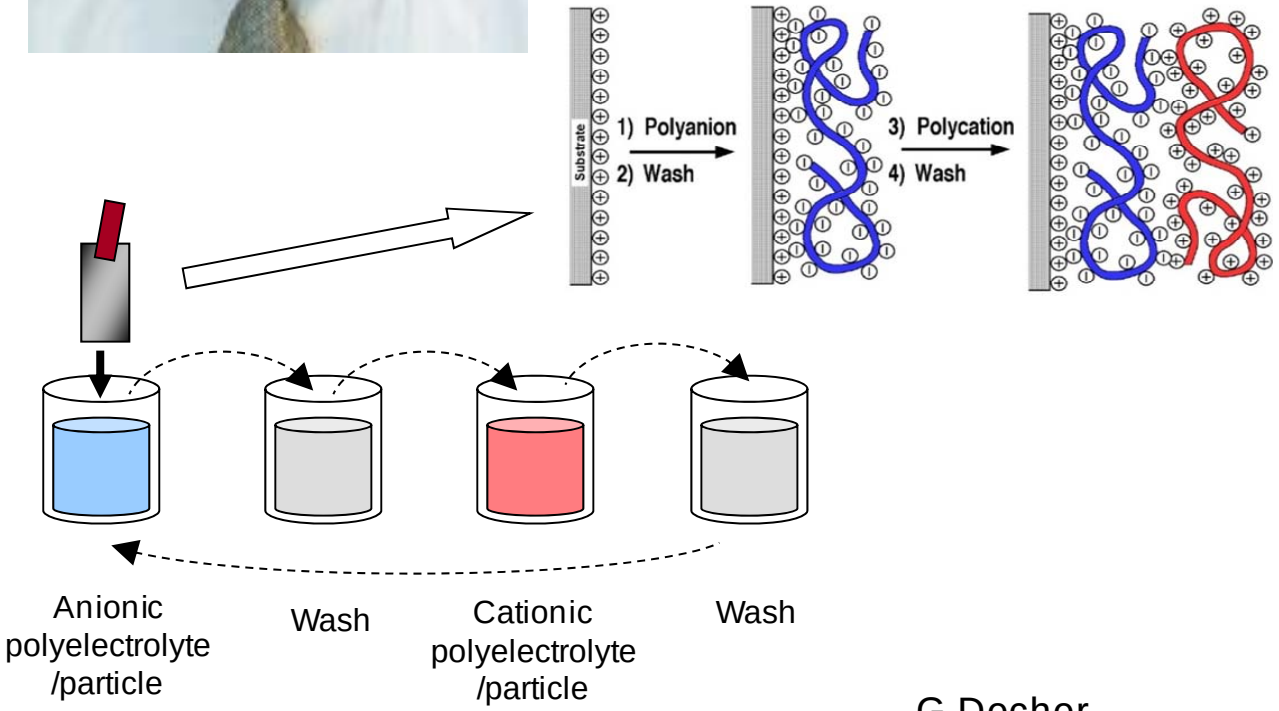
Design and characterization of free-standing films of nanofibrillated cellulose by the Layer-by-Layer Technology

Erdem Karabulut & Lars Wågberg
KTH Fibre and Polymer Technology



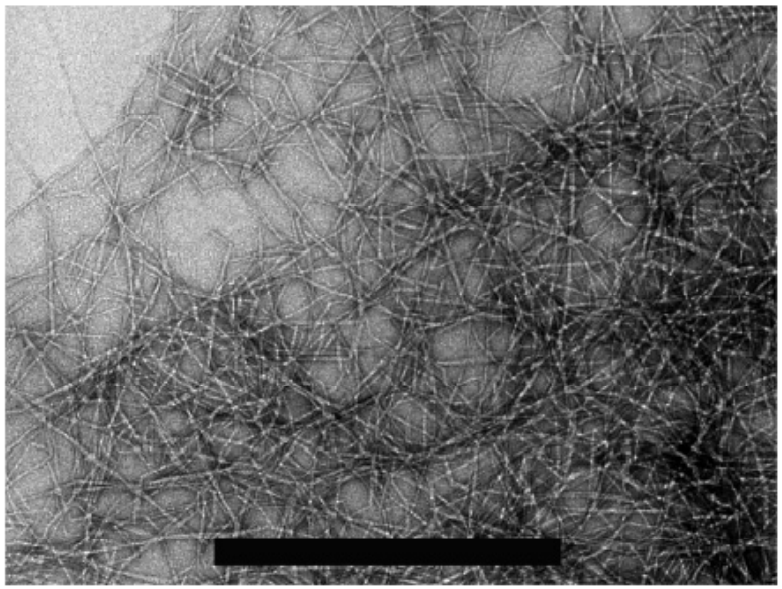
Free-standing LbL film of PEI and NFC (150 bilayers)

Professor Gero Decher
WP-4 Leader

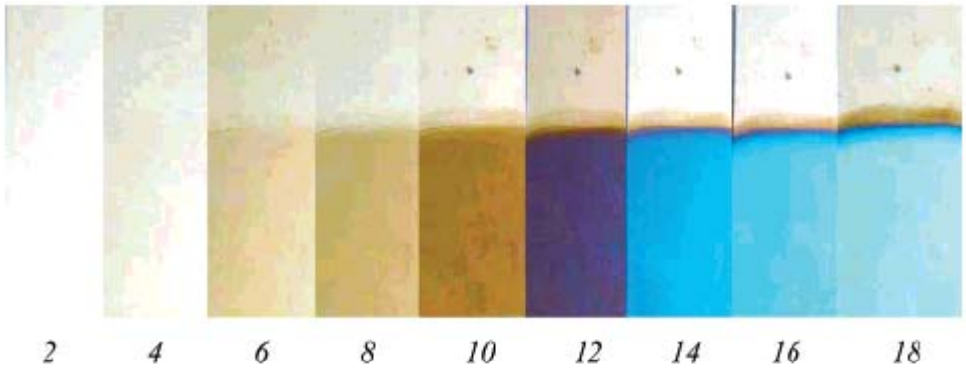


G Decher,
Science 277, 1232 (1997)

LbLs of NFC and polyelectrolytes



Wågberg et al
Langmuir 24(2008) 784-795



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Objective with LbL films;

A base for how to construct NFC/polyelectrolyte freestanding films for further modifications to high flux membranes

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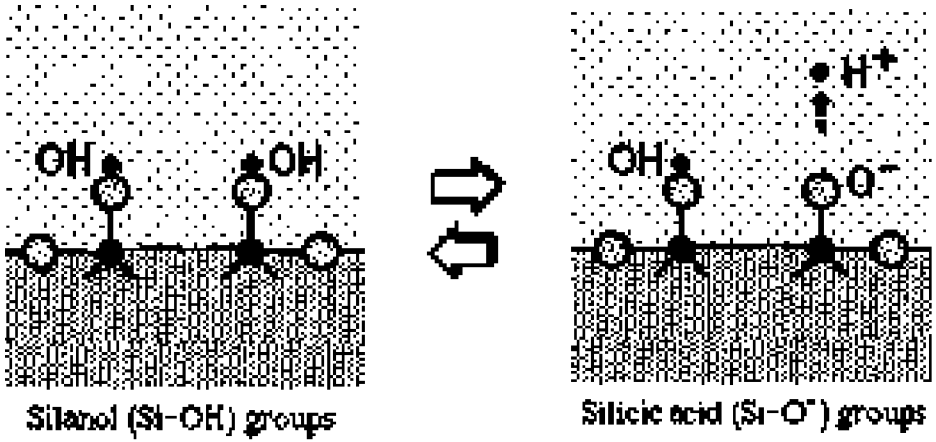
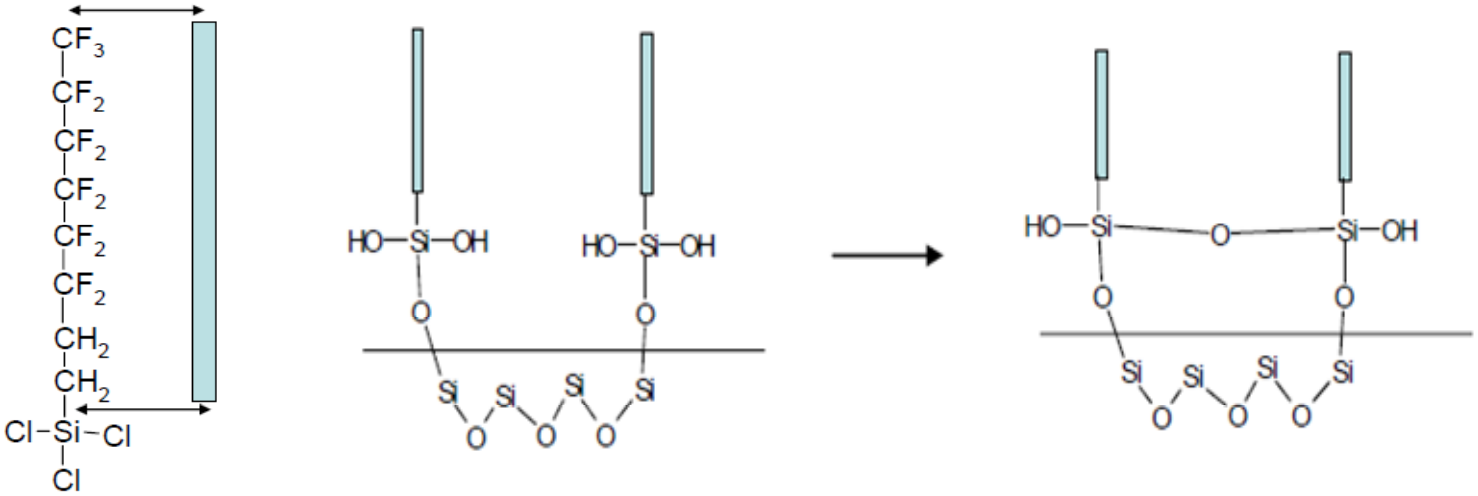
Silica and PFOS modified silica



Trichloro (1H,1H,2H,2H-perfluorioctyl) silane (PFOS)



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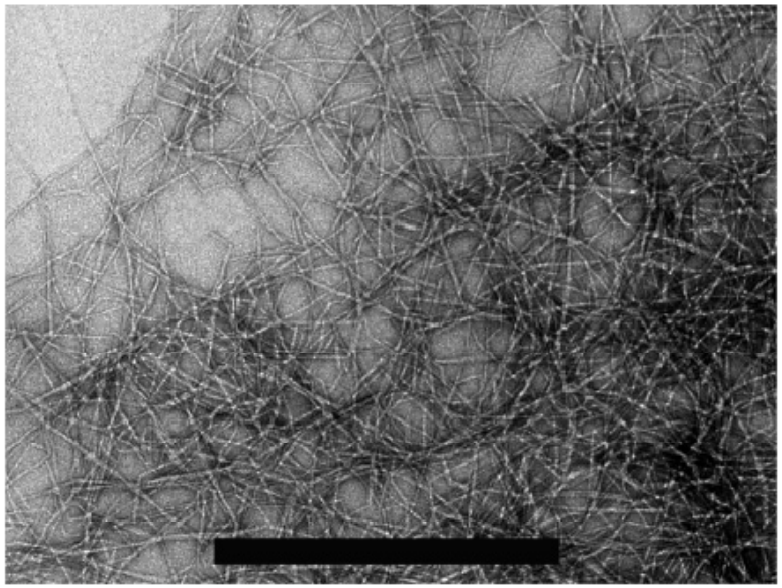
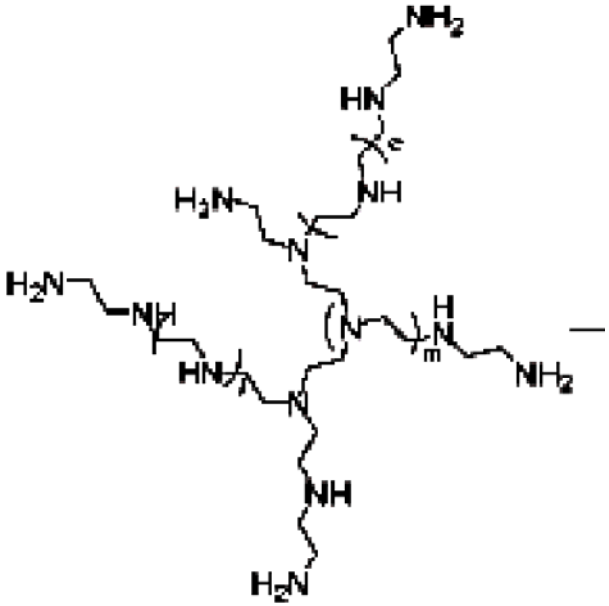
LbL-Materials

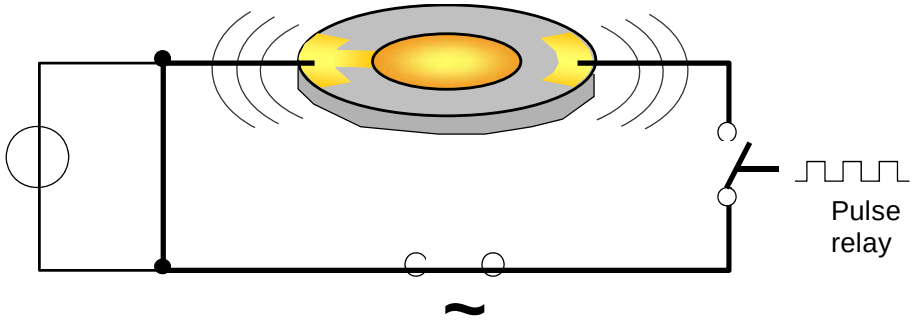




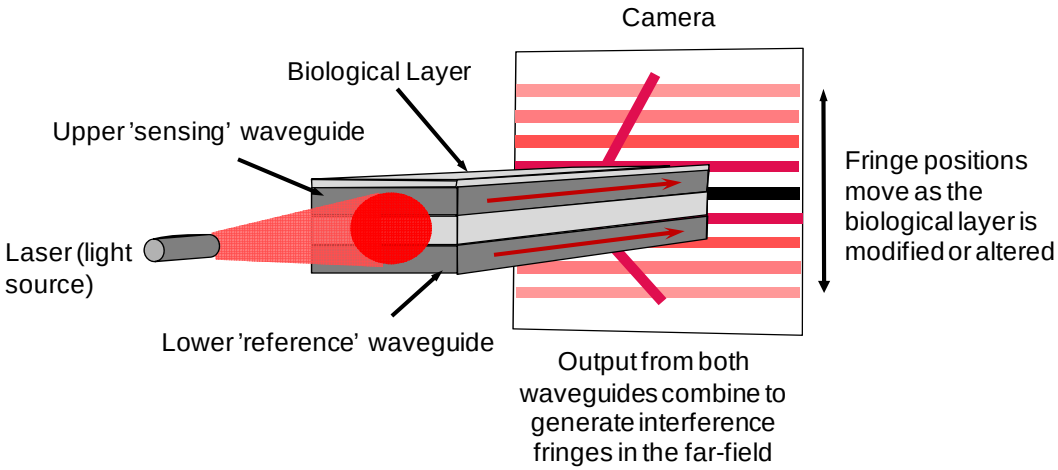
Techniques

QCM-D

Quartz crystal oscillating
due to the piezoelectric effect



DPI



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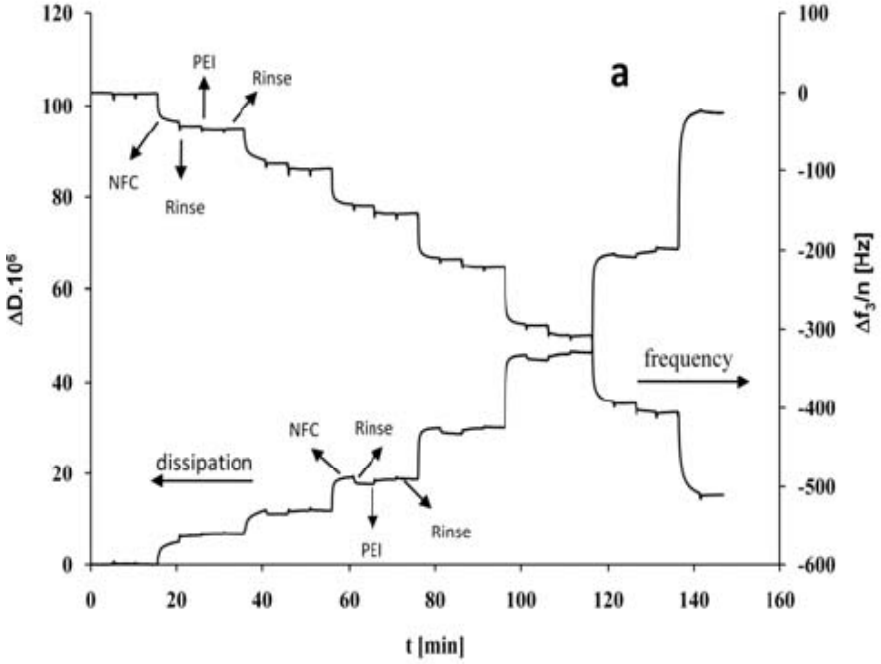
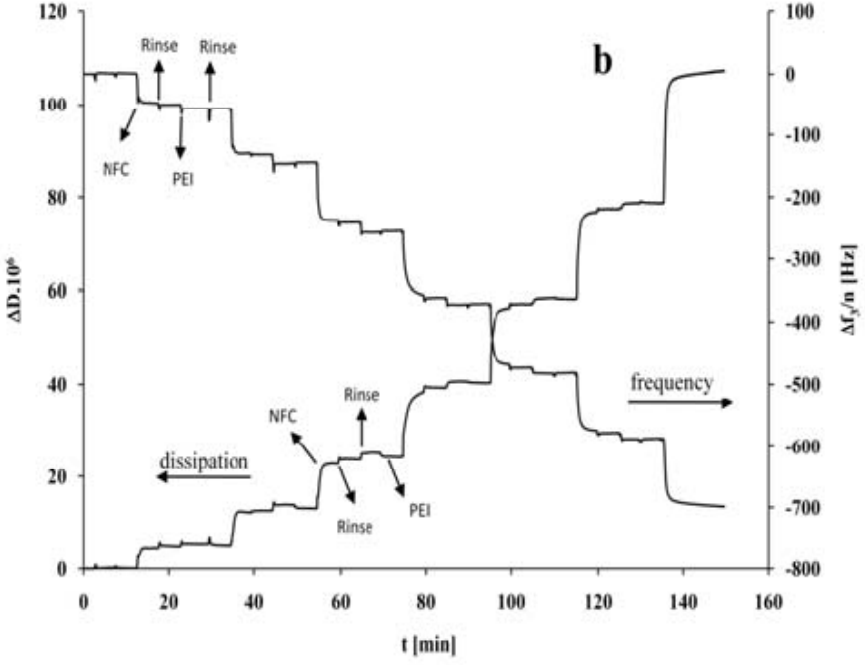
Silica

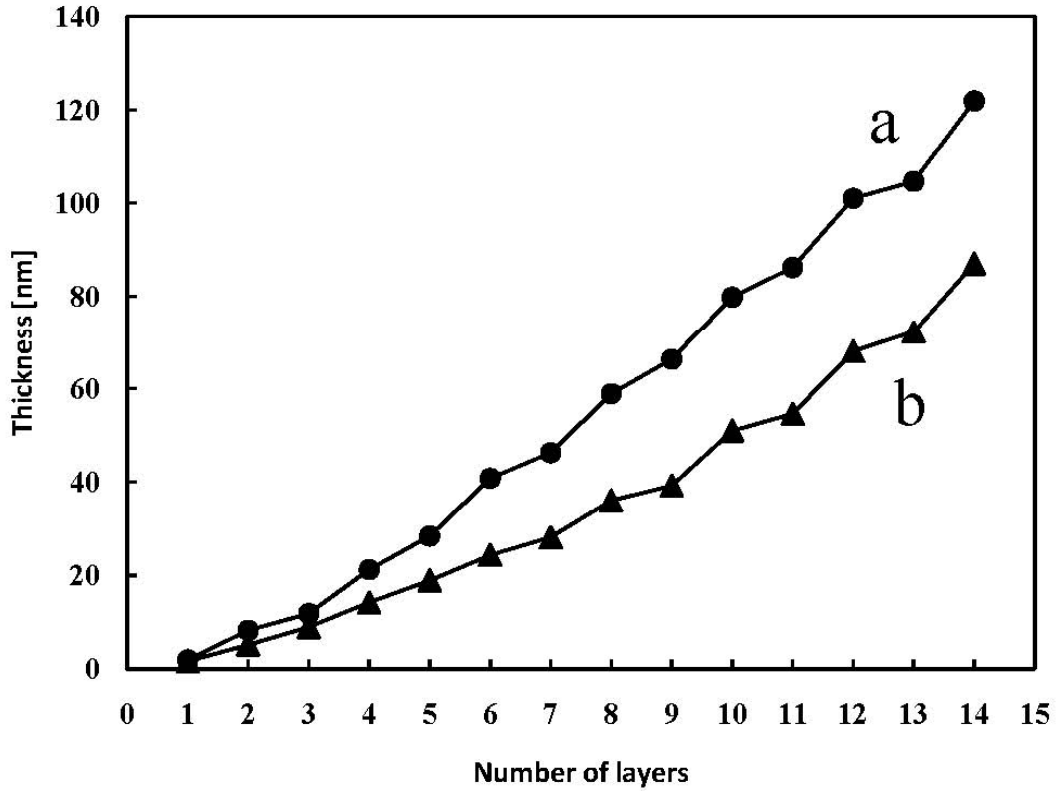


PFOS treated Silica



The build-of $(PEI/NFC)_7$ multilayer film on (a) non-coated, (b) PFOS-coated quartz crystals. Left and right *y*-axes show the chance in energy dissipation and normalized frequency (by considering the 3rd overtone) respectively, whereas the small arrows represent NFC-PEI introduction and rinsing steps.

Thickness development for silica and PFOS-treated silica



The estimated thickness of the $(PEI/NFC)_7$ multilayer film fabricated on (a) a PFOS-coated and (b) a hydroxylated bare silicon surface

The adsorbed mass and entrapped water content in each layer of $(PEI/NFC)_5$

Layer no	Adsorbed mass calculated with Eq. 1 (mg/m^2)	Adsorbed mass calculated with Eq. 2 (mg/m^2)	Change in water content (mg/m^2)	% water
1	0.47	0.44	0.03	6.40
2	6.25	2.78	3.47	55.5
3	1.76	0.67	1.09	62.0
4	7.18	3.93	3.25	45.3
5	1.87	0.86	1.01	54.0
6	8.29	4.67	3.62	43.7
7	1.57	0.89	0.68	43.3
8	9.94	4.22	5.72	57.5
9	2.09	0.86	1.23	58.9
10	12.71	3.43	9.28	73.0
Total mass	52.13	22.75	29.38	56.2[a]

[a] Total percent of associated water in $(PEI/NFC)_5$ film.

$$m = C\frac{\Delta f}{n} \quad \text{(Eq. 1)}$$

$$\Gamma = d_f \frac{n_f - n_b}{dn/dc} \quad \text{(Eq. 2)}$$

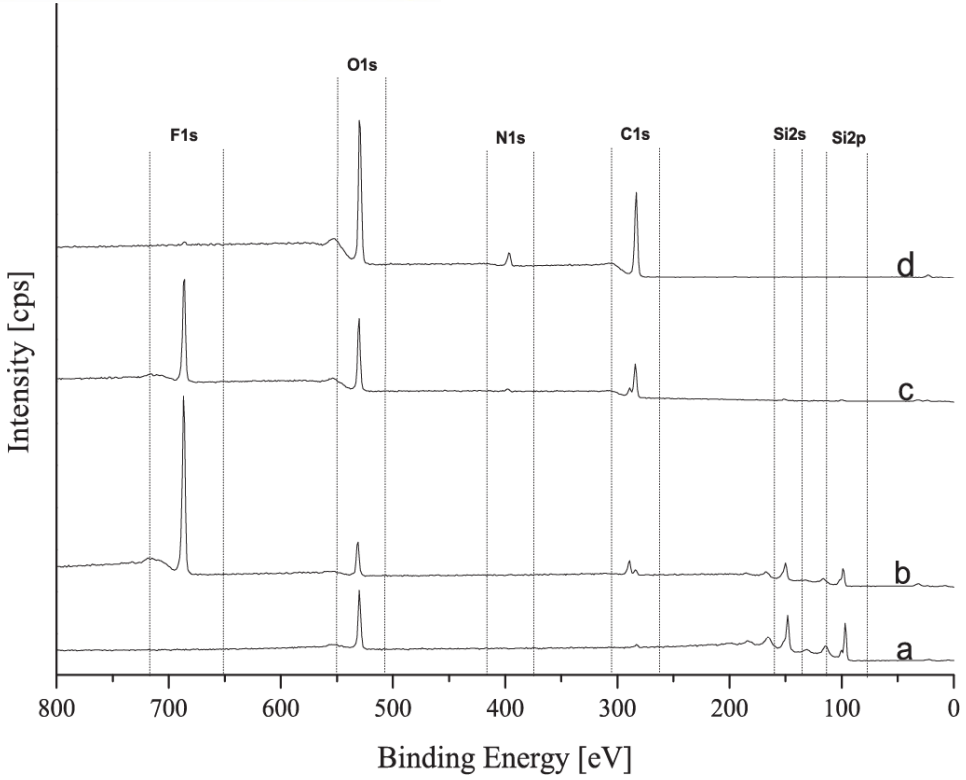
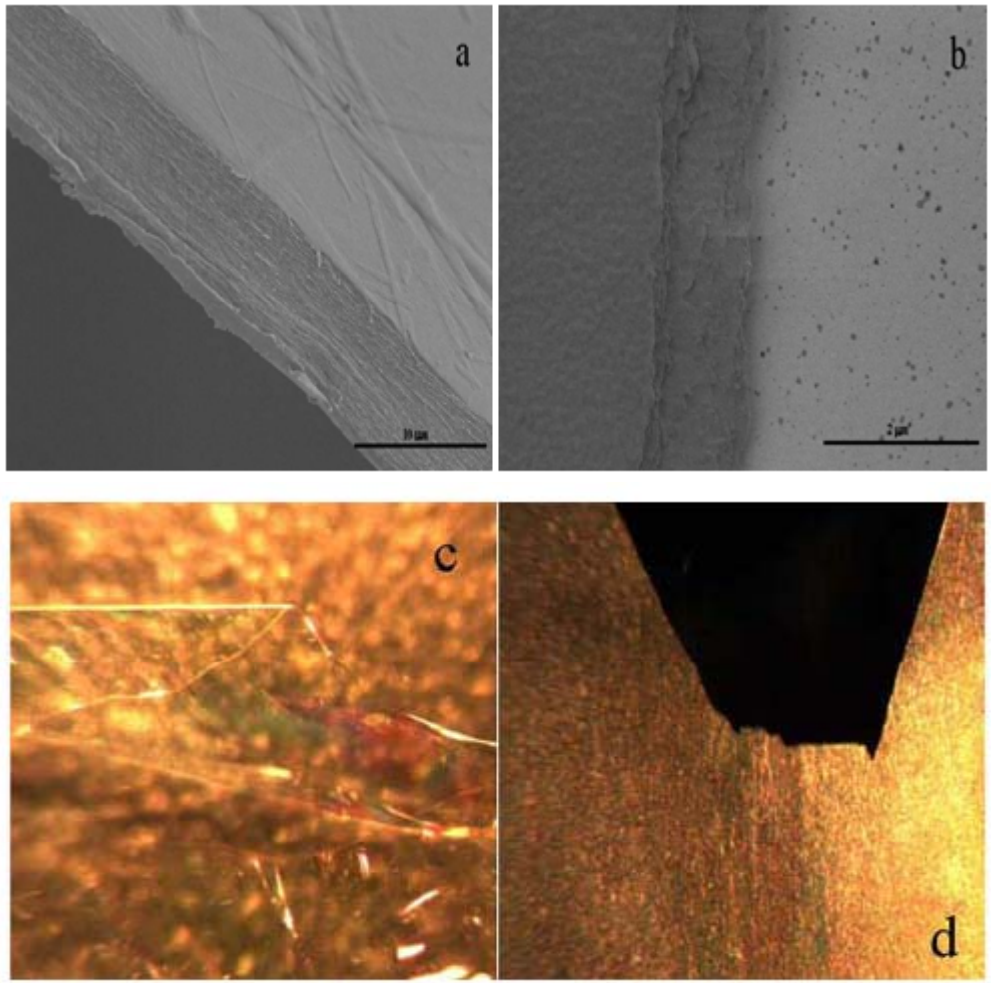


Fig. 2 XPS survey spectra of (a) bare, (b) PFOS treated (c) $(PEI/NFC)_3$ deposited on PFOS coated surface, (d) $(PEI/NFC)_{10}$ deposited on PFOS coated surface.

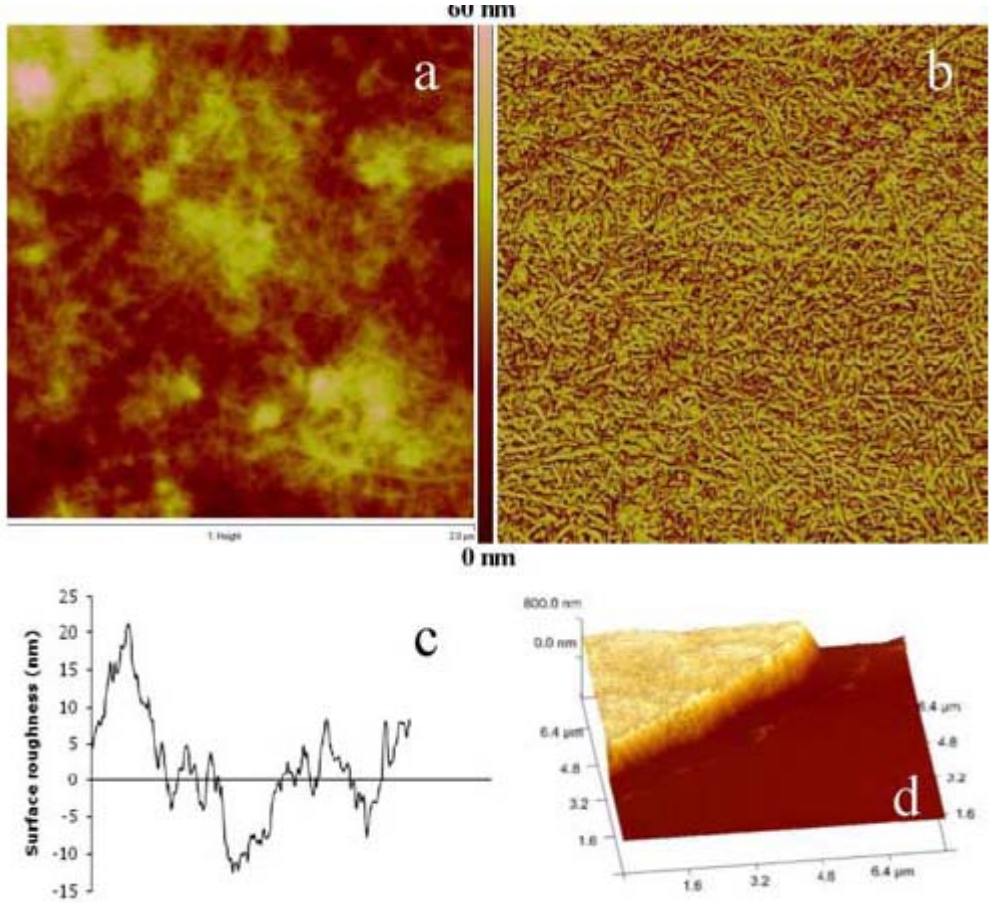
Substrate type	Atomic surface concentrations [a] (%)				
	C	O	Si	F	N
Bare silicon substrate [b]	4.7	25.7	69.7	-	-
PFOS treated silicon substrate	26.2	10.8	26.2	36.8	-
$(PEI/NFC)_3$ deposited on PFOS coated substrate	50.4	21.6	2.1	23.9	1.7
$(PEI/NFC)_{10}$ deposited on PFOS coated substrate	65.1	29.4	-	-	5.4

[a] Atomic surface concentrations were calculated by integrating the areas under the peaks. [b] Reference atomic concentration.

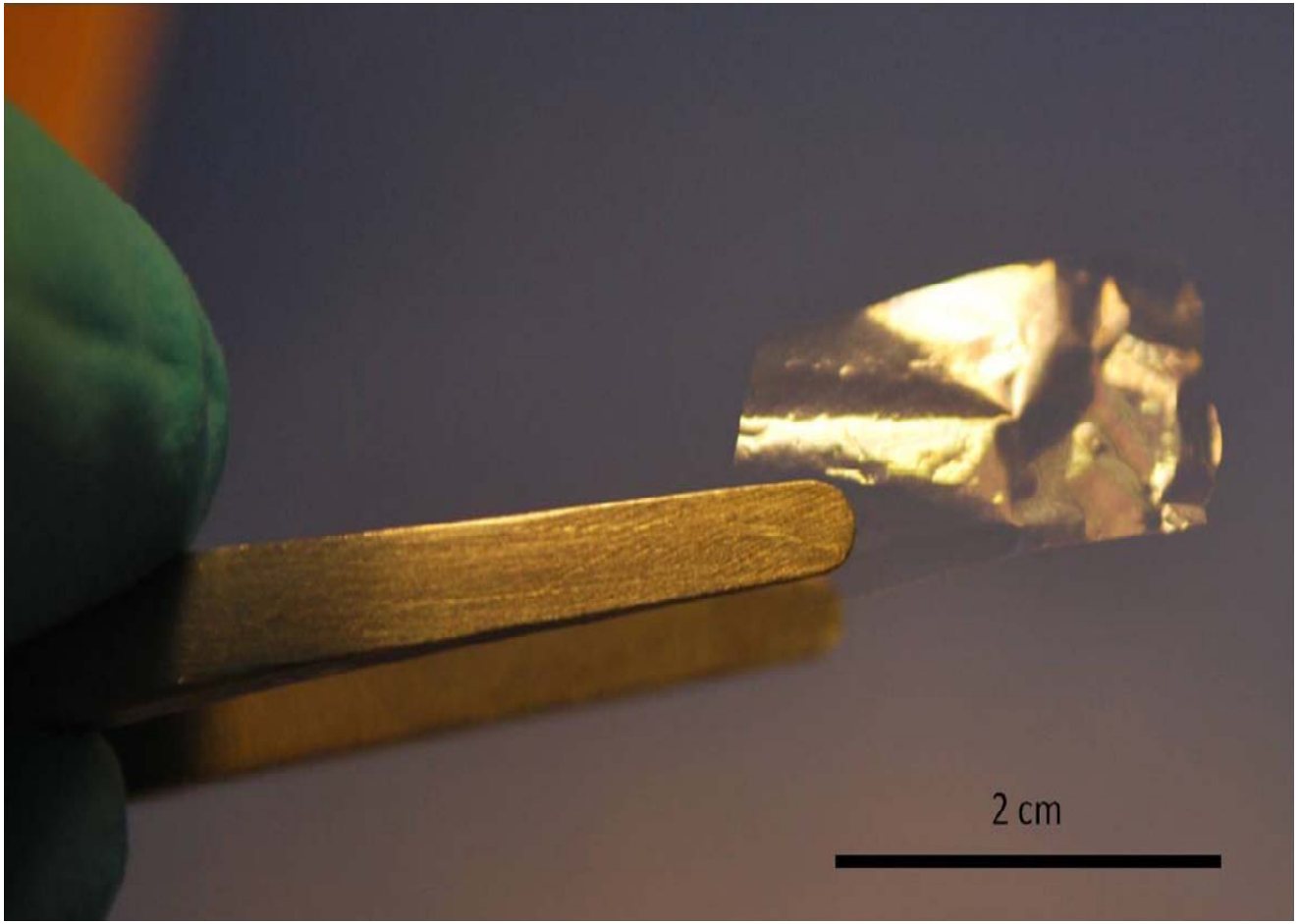
Atomic surface concentrations of different surfaces determined by XPS



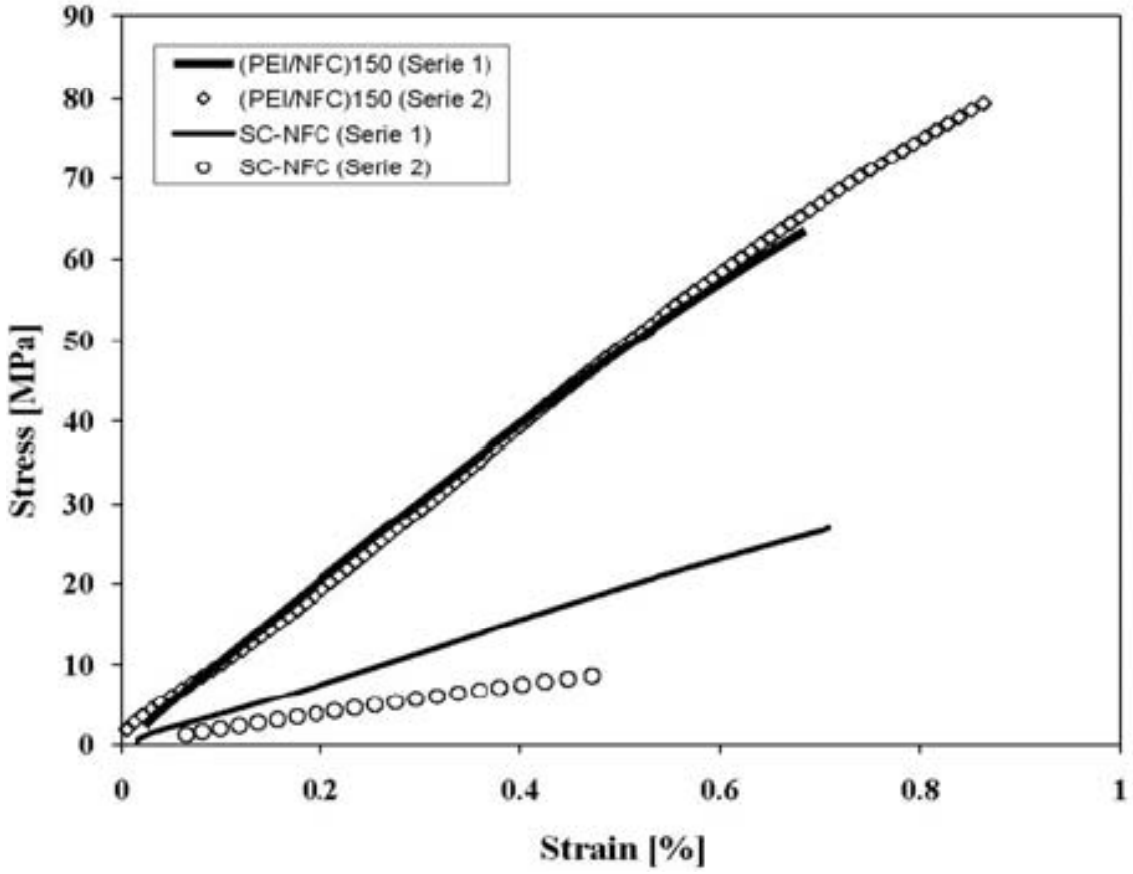
High-magnification (x4000 and 15000, respectively) stratified cross-sectional FE-SEM images of (a) $(PEI/NFC)_{150}$ and (b) $(PEI/NFC)_{40}$. The scale bars are 10 and 3 mm, respectively. The thickness of $(PEI/MFC)_{150}$ was measured as 5.8 mm. Relatively large fibrillar entities exist at the outermost layer of the film. Optical microscopy images of (c) $(PEI/NFC)_{30}$ and (d) $(PEI/NFC)_{40}$ where the black part is the bare silicon substrate after film removal.



AFM tapping-mode, (a) height and (b) phase images of $(PEI/NFC)_{20}$ on silica substrate. The scanned surface area was 4 mm^2 and the *z* range was 25 nm. (c) typical surface height profile of $(PEI/NFC)_{20}$. The average surface roughness was found to be 8.95 ± 0.10. (d) 3D surface morphology of $(PEI/NFC)_{25}$ after peeling-off a piece of the LbL film on silica substrate. The cross-sectional thickness of dry $(PEI/NFC)_{30}$ was measured as 400 ± 20 nm.


2 cm

Mechanical testing of free-standing films



Typical stress-strain curves of $(PEI/NFC)_{150}$ and SC-NFC films.

Mechanical properties of films

Mechanical properties of $(PEI/NFC)_{150}$ and SC-NFC free-standing films

Material	Serie number[a]	Thickness from FE-SEM (µm)	Young`s modulus (GPa)	Strength (MPa)	Strain at break (%)
$(PEI/NFC)_{150}$	1	5.16 (± 0.08)	9.37 (± 2.0)	80 (± 8)	0.86 (± 0.05)
	2	5.30 (± 0.08)	9.36 (± 2.0)	63.5 (± 6)	0.68 (± 0.04)
SC-NFC	1	6.83 (± 0.10)	3.84 (± 1.0)	26.8 (± 2)	0.70 (± 0.05)
	2	6.95 (± 0.10)	1.83 (± 1.0)	8.6 (± 0.8)	0.47 (± 0.03)

[a] each serie contains three speciments with the same dimensions and the presented results are the average of these measurements.

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Conclusions

- We can form LbL films of NFC and cationic polyelecytrolytes/nanoparticles on silica and PFOS modified silica
- The composition of the films can be tailored and analysed with the used techniques
- Ultrathin films can be peeled off from the PFOS treated silica surfaces

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Future

- Chemical modification of the fibrils to tailor the properties of the ultrathin films
- Preparation of NFC/nanoparticle films where the particles are dissolved away to control the porosity and the size of the pores in the films
- Combinations with fibrillar aerogels/foams

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Thank you for listening!! Questions??