Combinatorial QCM-D/GE-Study of Protein Adsorption on Polymer Brushes grafted to Nanostructured Surfaces

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functional hybrid materials with stimuli-responsive properties

Monitoring of functional characteristics by combinatorial QCM-D/GE

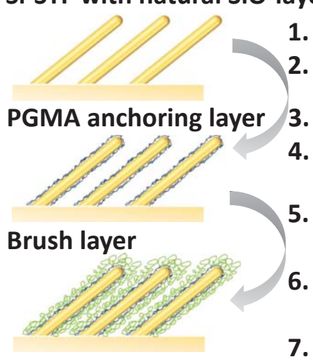
Protein adsorbing and non-fouling nanostructures → drug delivery, tissue engineering and sensing applications

Sample Preparation

- glancing angle deposition of silicon onto substrates
- electron beam evaporation
- oblique angle shadowing to create slanted columnar morphology(1)

Polymer Brush Preparation by 'Grafting To' approach(2)

Si-STF with natural SiO-layer



1. **Cleaning** with Ethanol
2. **Cleaning and Activation** with O_2-Plasma
3. **Spin-Coating** 0.02wt-% PGMA in MEK
4. **Annealing in vacuum** 10 min, 110°C

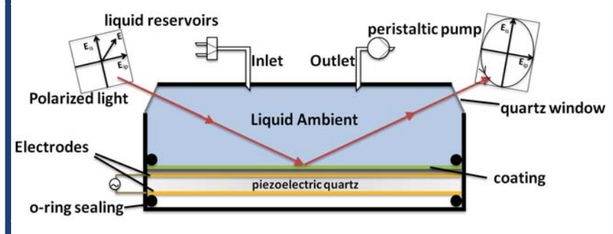
PGMA= Poly(glycidyl methacrylate) M_w=17 500 g/mol, M_w/M_n=1.7

5. **Spin-Coating** 1wt-% PAA in Ethanol / 1wt-% PNIPAAm in $CHCl_3$
6. **Annealing in vacuum** PAA: 30 min, 80°C (Guiselin Brushes) / PNIPAAm: 16h, 150°C
7. **Extraction in Ethanol** 30 min

PAA= Poly(acrylic acid): M_w=26 500 g/mol, M_w/M_n=1.12
PNIPAAm= Poly(N-isopropylacrylamide): M_w=56 000 g/mol, M_w/M_n=1.14

Measurement

Quartz Crystal Microbalance with Dissipation Mode (QCM-D) + **Generalized Ellipsometry (GE)**

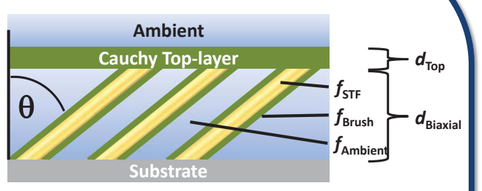


- **simultaneous insitu experiments**
- **characterization of changes in optical and mechanical properties**

Modeling

GE

anisotropic Bruggeman effective medium approximation(3)



Ambient: Air, DI water or Buffer solution
Cauchy Top-layer : thickness d_{top} fixed refractive index A=1.5, B=0.01
f_{STF}: slanted thin film fraction (composed of Si/SiO_2)
$f_{ambient}$: ambient fraction
f_{Brush}: polymer brush fraction, fixed refractive index A=1.5, B=0.01
$d_{Biaxial}$: biaxial thickness
θ : column slanting angle
Substrate: Silicon

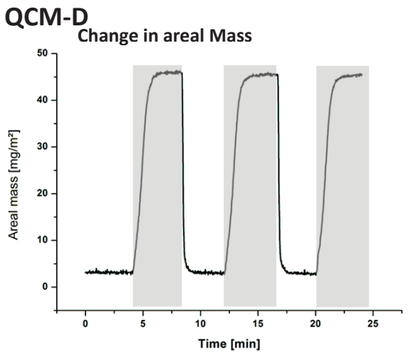
QCM-D

Viscoelastic modeling by Voigt-Voinova-Approach(4)

Thickness, mass and viscoelasticity of thin films
- **fixed layer density δ=1g/cm³**

Stimuli-responsive swelling of Polymer Brushes on STF

pH sensitive PAA Brushes

QCM-D


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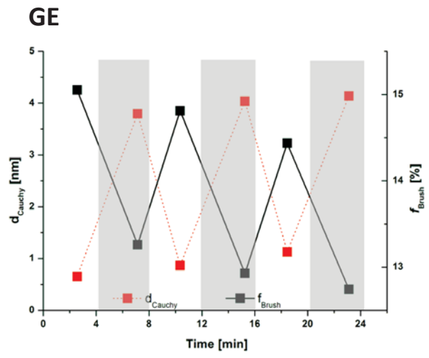
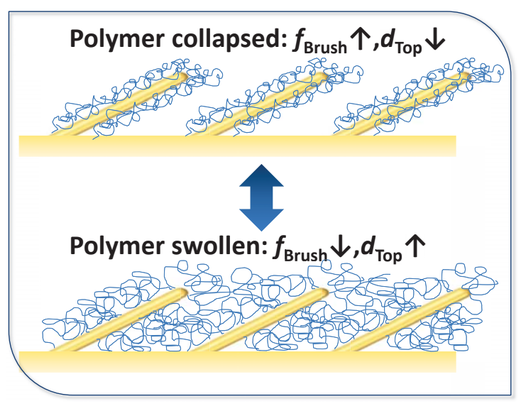
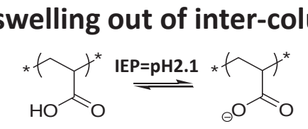


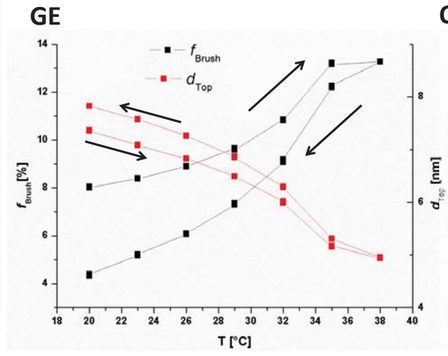


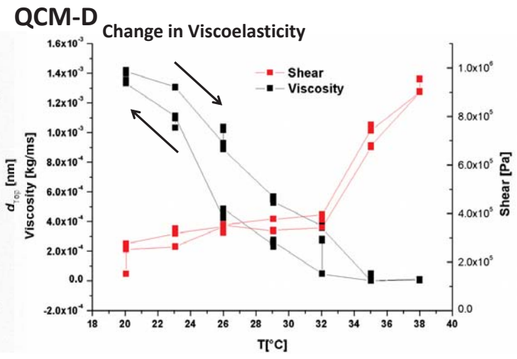
Acetate Buffer
c(Na^+)=0.01M
Light areas: pH3.7
Shaded areas: pH7.3
QCM-D Raw Data offset to deswollen state

PAA swells with increasing pH
- **incorporation of counter ions, increase in areal mass**
- **increase in viscoelasticity**
- **partly swelling out of inter-columnar space**



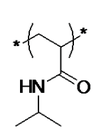
T sensitive PNIPAAm Brushes

GE


QCM-D


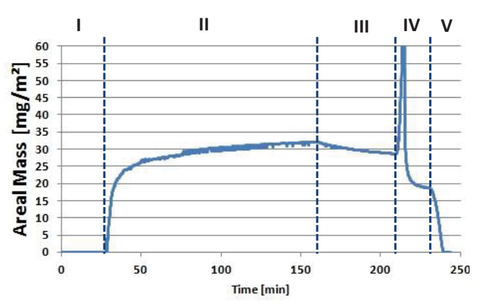
DI water
- QCM-D Raw Data offset to deswollen state,
- subtraction of bare sensor T-dependence,
- density and viscosity of ambient varied with T (5)

PNIPAAm deswells with increasing T: LCST at ~32°C
- **loss of counter ions, decrease in areal mass and viscoelasticity**
- **partly deswelling back into inter-columnar space**
- **cooling ≠heating due to inter- and intra-chain hydrogen bonds**
- **transition broader than on flat surface**



Protein Adsorption on Polymer Brushes on STF

Protein-adsorbing PAA Brushes

QCM-D


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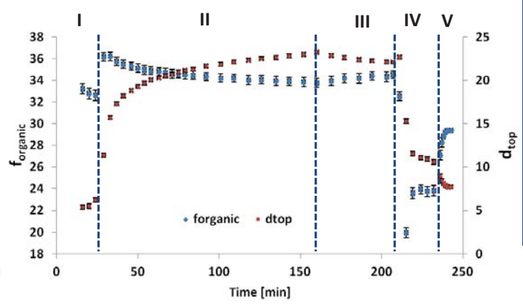
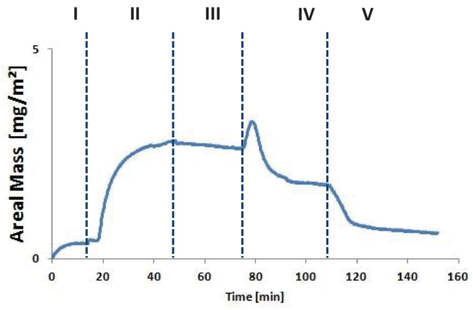


Phosphate Buffer
c(Na^+)=0.01M

I: rinse with pH5
II: adsorption BSA (0.25 mg/ml in pH5)
III: rinse with pH5
IV: rinse with pH7.4
V: rinse with pH5

- **pH5: high adsorption and retention**
- **pH7.4: fast desorption** (higher electrostatic repulsion between BSA and PAA, desorption and swelling of polymer at the same time)
- **protein mostly adsorbed in top layer**
- **adsorbed amount similar to adsorption on PAA on flat surface,**
  → possible reason: high slanting angle (~80°)

Protein-resistant PNIPAAm Brushes

QCM-D (Sauerbrey modeling for rigid layer)


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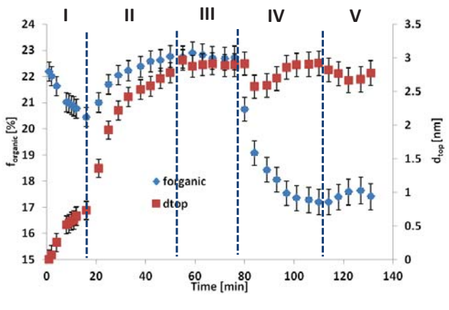

- **Almost no protein adsorbed** (STF without Brush → ~10mg/m²)
- **pH7.4: desorption** (higher net charge of protein, IEP_{BSA}=5.6)
- **rearrangement of polymer during desorption :** decrease in $f_{organic}$ while d_{top} constant
- **QCM-D: second loss of mass at pH5** (dehydration of remaining protein)

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