Formation and spectroscopic analysis of conditioning films on self assembled monolayers

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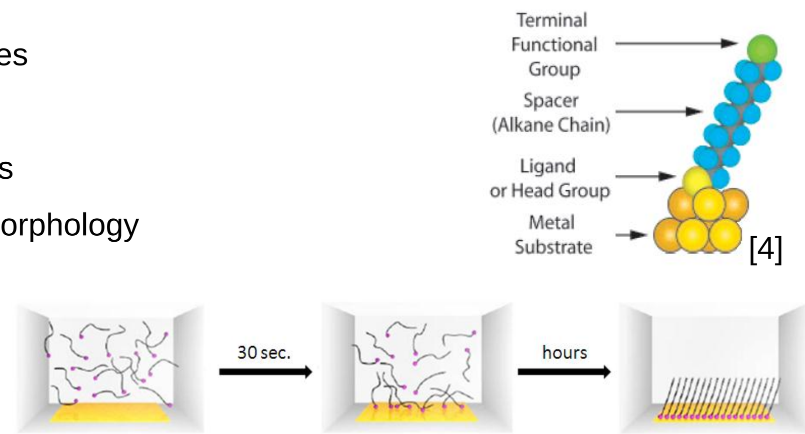
INTRODUCTION

Biofouling

- undesired growth of marine organisms on submerged structures and devices
- ubiquitously occurring phenomenon in intertidal zones worldwide [1]
- world fleet fuel consumption is 300 million tonnes higher due to fouling-induced rise in drag [2]
- to reduce the negative impact of biofouling, suitable non-toxic coatings for the marine environment are required
- our approach is to derive design rules for non-fouling coatings from well defined model surfaces with different surface chemistries and morphologies [3]

Self-assembled monolayers (SAMs)

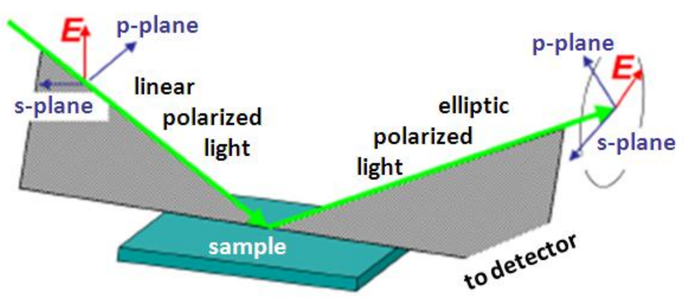
- providing access to highly controlled surface chemistries
- fine tuning of physicochemical surface properties
- highly versatile tools to create defined thin organic films
- changing the surface chemistry without affecting the morphology or its elastic modulus
- easy to prepare



TECHNIQUES

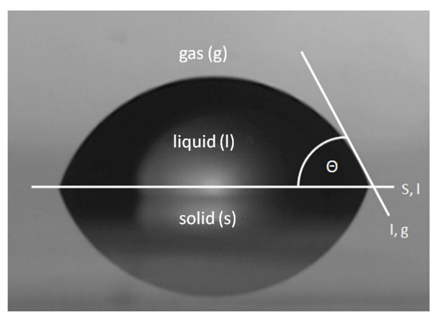
Ellipsometry

- measuring the thickness of the formed biofilms



Contact angle measurements

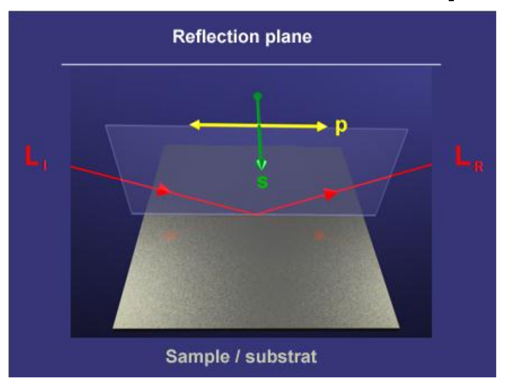
- measuring the hydrophobicity of the surfaces



Young's equation:

$$\cos\Theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

Infrared reflection adsorption spectroscopy (IRRAS)

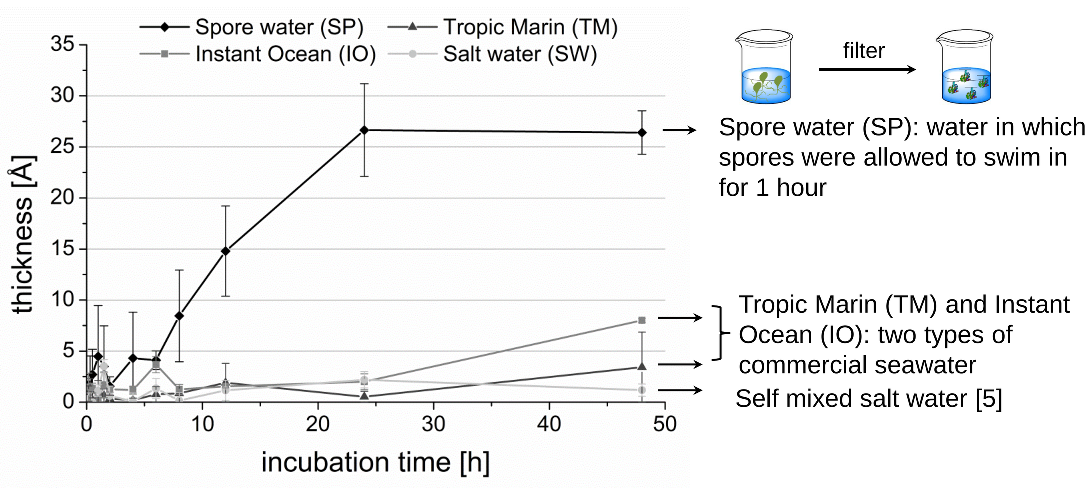


- reflection plane is defined by incident and reflected beam
  - p-polarized light: polarization direction parallel to reflection plane
  - s-polarized light: polarization direction perpendicular to reflection plane
- only p-polarized light is absorbed by thin layers on metal substrates
- only molecules with perpendicular dipole change to surface interact with incoming light
- strongest absorption is theoretically given by an angle of incidence of 80°

CONDITIONING FILMS

Conditioning by different types of seawater

- dodecanthiol SAM (C12) as test surface
- different types of commercial seawater, self made seawater and 'spore water' (ASW where spores had been swimming for 1 h)
- incubate samples in different types of water for different time periods

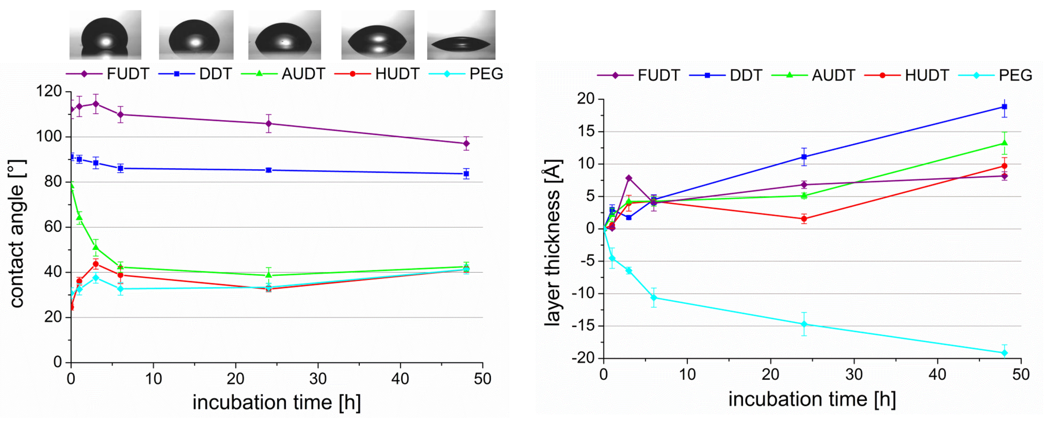


- only spore water shows film accumulation of proteins
- all other types of seawater show slightly accumulation of proteins

conditioning film is enhanced by traces of macromolecules, which are released from swimming spores kept suspended for 1 h

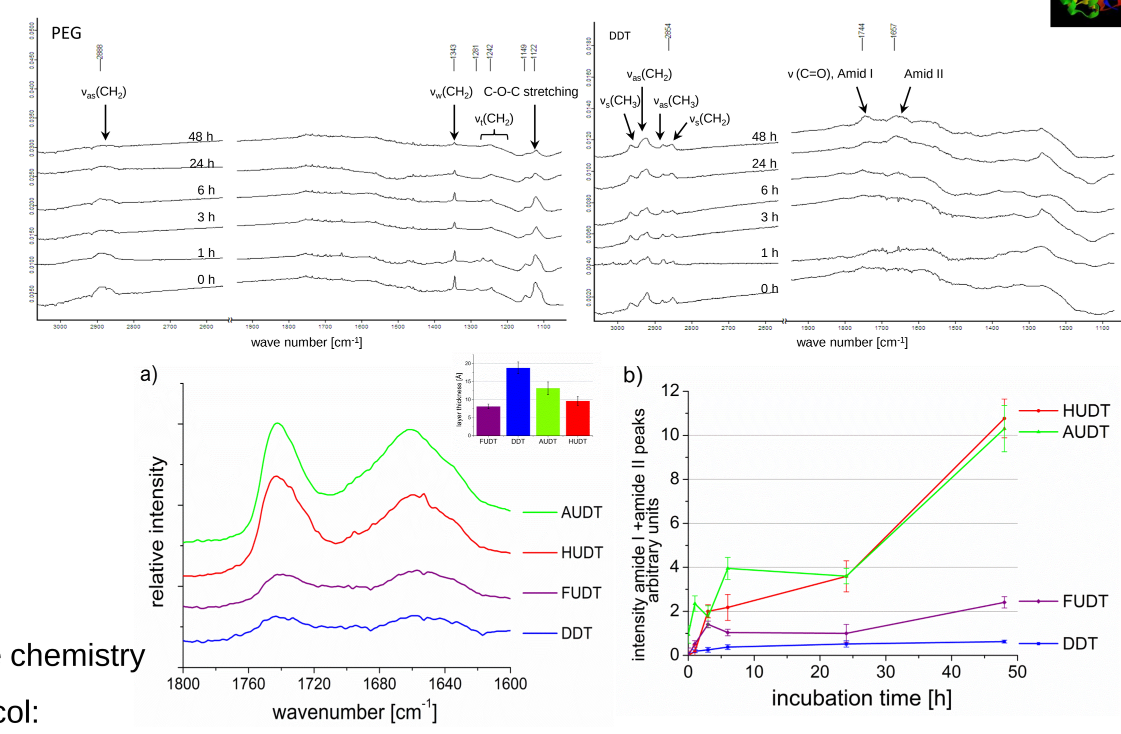
Conditioning of surfaces by 'spore water'

- experiments in 'spore water' with chemically different surfaces
- ellipsometric and contact angle measurements



- for all surfaces contact angles change with time
- thickness of conditioning layers increases with time independently of the surface chemistry
- PEG 2000-OH deteriorates with time in seawater, typical IR peaks (ethylene glycol: ~1122-1343 cm^{-1}, CH_2 peaks: ~2888 cm^{-1}) disappear but the surface stays free of proteins
- chemically different samples in 'spore water' show accumulation of amide containing macromolecules, e.g. proteins (amid I (~1750 cm^{-1}) and amid II (~1650 cm^{-1}) bands)
- intensity of SAM peaks (~ 2888 cm^{-1}) remains unchanged
- significant conditioning is established after ~24 hours

FT-IR measurements

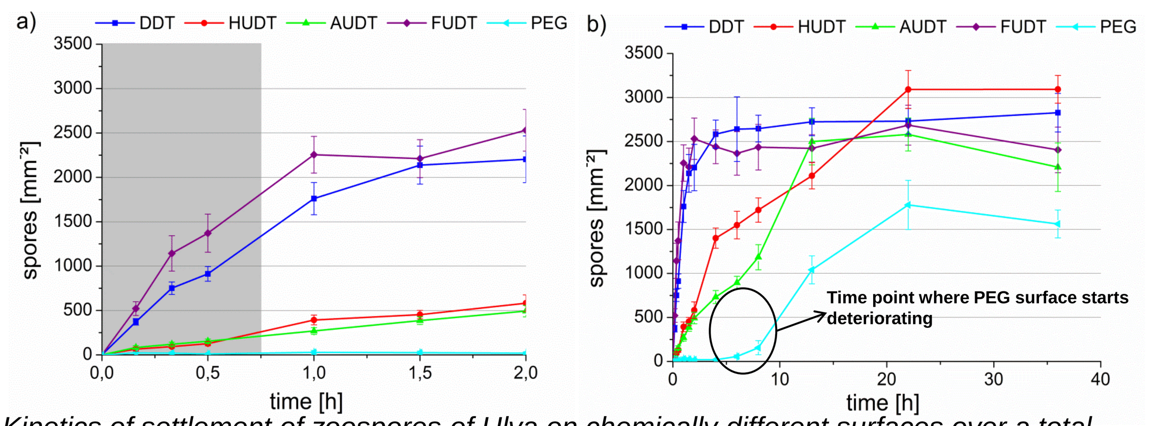


Amid I and amid II intensity on all different surfaces conditioned by spore water (SP). a) amid bands after 48 hours, b) calculated intensities of amid bands..

How does the time scale for conditioning and settlement of spores correlate?

KINETICS

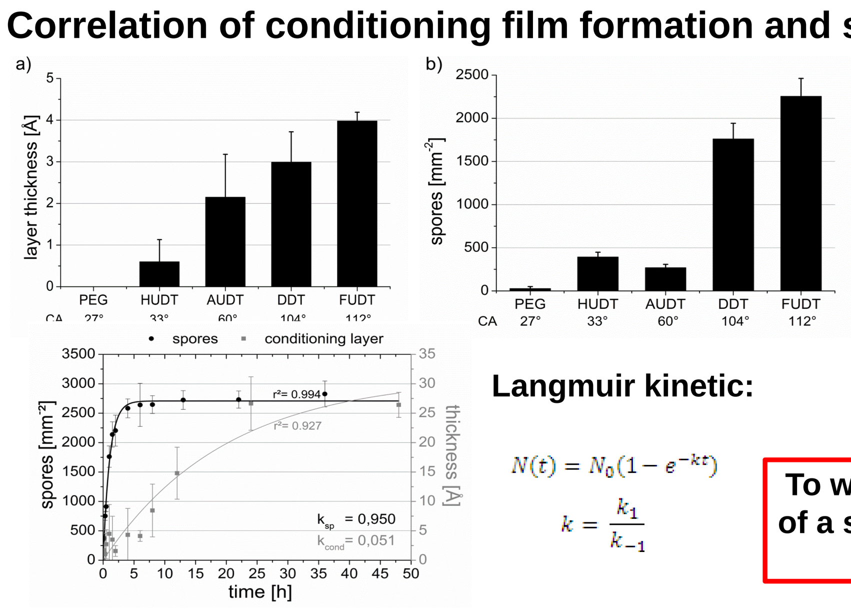
Kinetic studies



Kinetics of settlement of zoospores of Ulva on chemically different surfaces over a total duration of 36 h.
a) Initial time up to 2 hours, the area in grey represents the usual time for a spore assay
b) settlement of spores up to a total settlement time of 36 h.

- settlement (except on PEG) saturates at approximately the same value after ~20 h
- at an essay time of 60 min the surfaces' coverage is best distinguishable
- PEG 2000-OH surface is resistant against spore settlement for about 10 hours before degradation changes the surface properties
- settlement could be combined effect of surface chemistry and formation of a conditioning layer

Correlation of conditioning film formation and spore settlement after 1 hour



Langmuir kinetic:

$$N(t) = N_0(1 - e^{-kt})$$

$$k = \frac{k_1}{k_{-1}}$$

- saturation and surface conditioning occurs on similar timescales
- but reaction rate is different k_{SP}=0.950 h^{-1} and k_{Cond}=0.051 h^{-1}

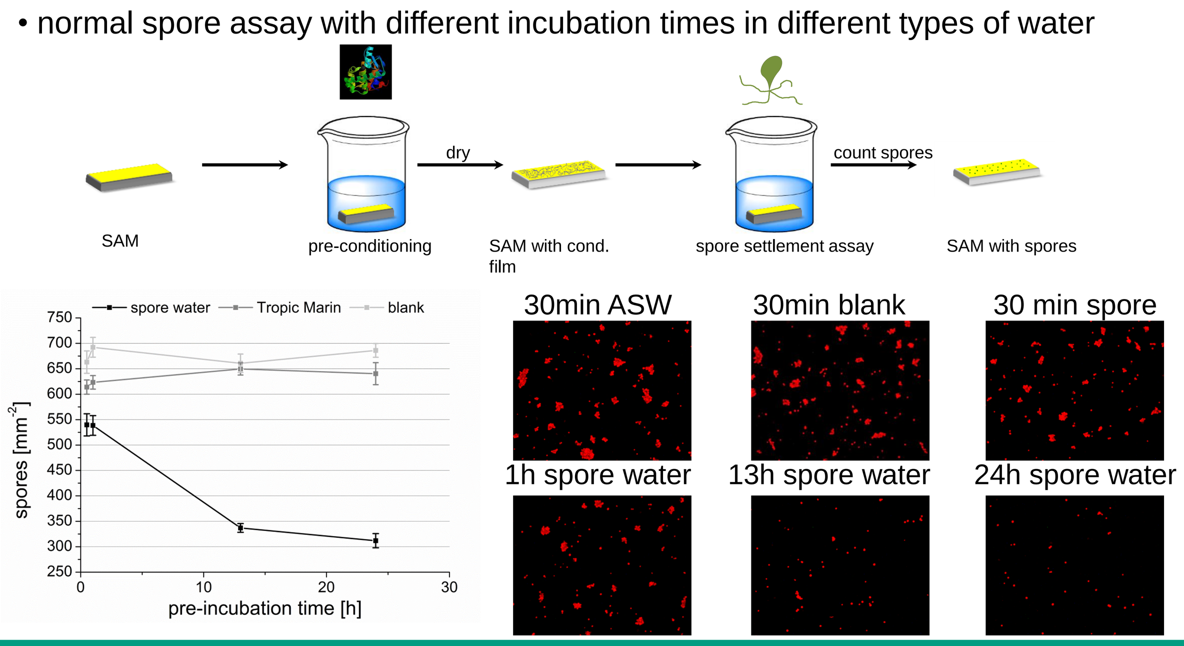
→ Spore settlement is much faster then conditioning of surface

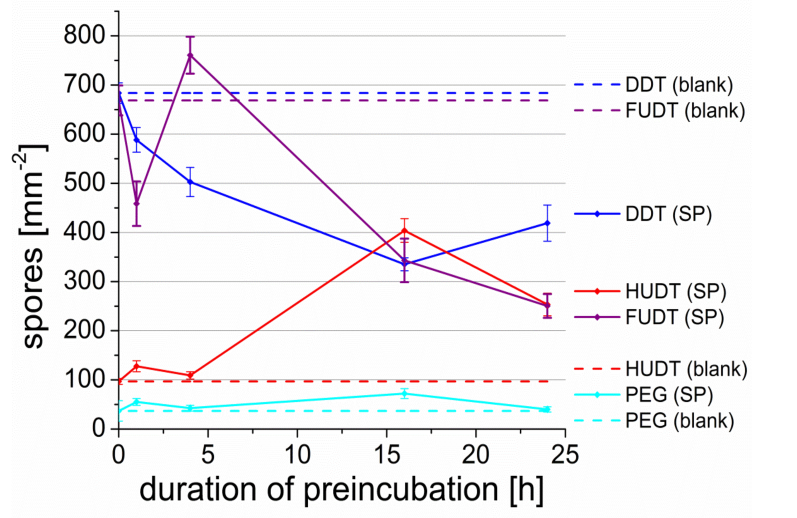
To which extend does the conditioning of a surface change the attachment rate during the settlement phase?

INFLUENCE

Influence of conditioning film on settlement of alga *Ulva linza*

- normal spore assay with different incubation times in different types of water



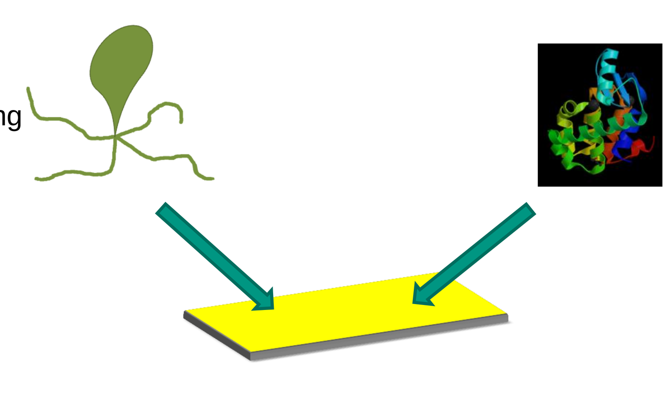


Settlement density of Ulva spores on SAMs after varying durations of pre-incubation in either spore water (SP, solid lines) or without pre-incubation (blank, dotted lines).

- for hydrophobic surfaces incubation leads to decrease in spore density
- for hydrophilic surfaces the settlement density is growing with pre-incubation time
- pre-incubation with 'spore water' influences spore settlement already before the conditioning film is fully established
- reason is change of surface properties as a result from adsorption of proteins and other dissolved organic carbons (DOC)
- this DOC add layer deters spores from settling, e.g. by changing physical spore-surface interaction as a consequence of reducing surface energy
- distribution of settled spores changes from gregarious (clumped) to single spores and small groups with exposure to the conditioning solution

CONCLUSION

- conditioning film is formed on all surfaces
- composition of conditioning film depends on surface chemistry
- reaction rates show that spore settlement is much faster then surface conditioning
- conditioning film influences spore settlement
- surfaces get conditioned independent of the end group chemistry
- conditioning during the settlement phase changes the attachment rate



Conditioning of surfaces plays a role in lab assays
Conditioning and settlement are competitive events

LITERATURE

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