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# LAYER-BY-LAYER SELF-ASSEMBLY – A POWERFUL TOOL FOR MATERIALS INTEGRATION

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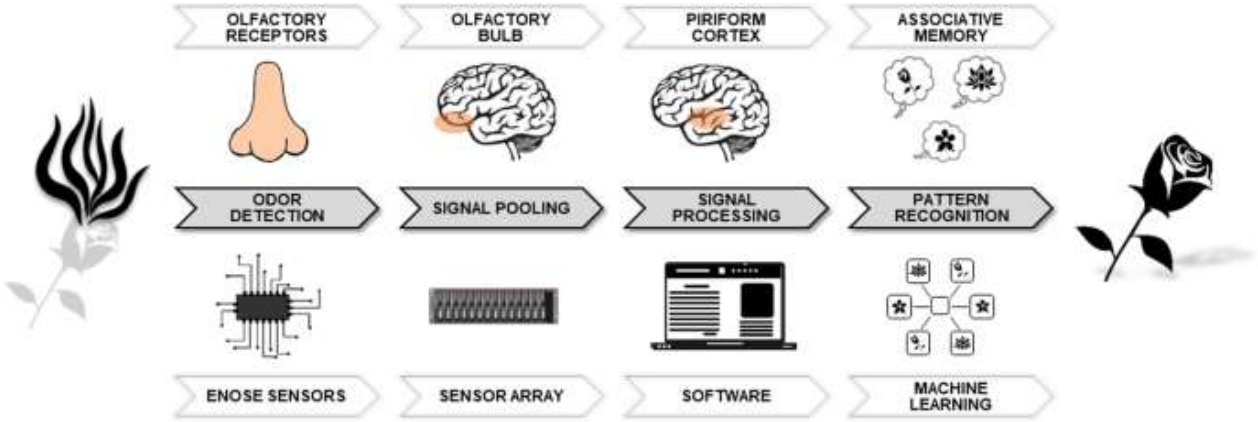
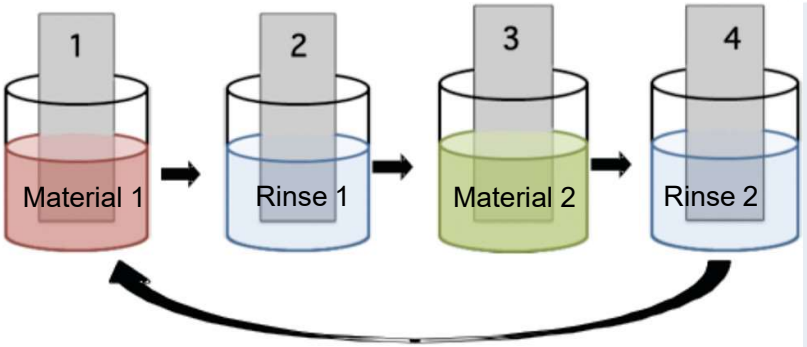
# Motivation

**Problem:** Integration of thin functional layers of composite materials into devices
e.g. for electronic noses



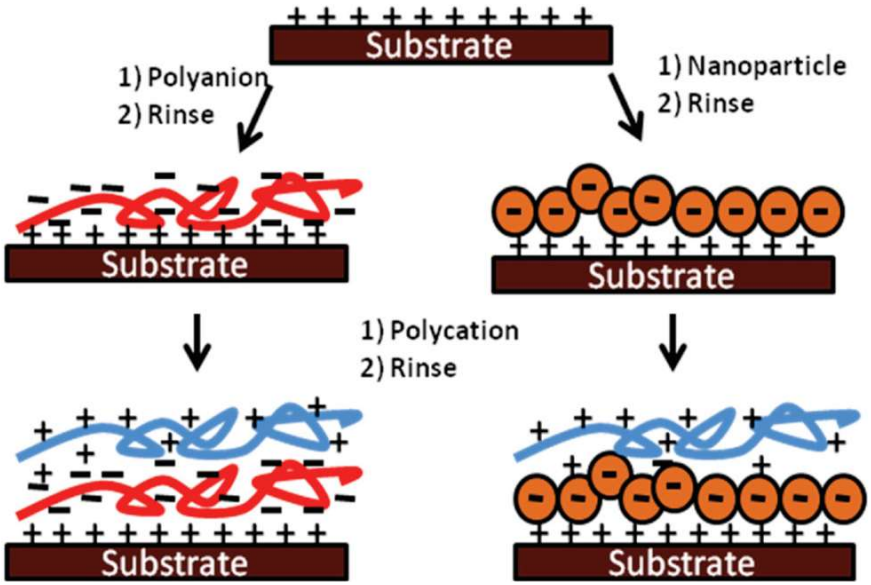

https://doi.org/10.1186/s12931-021-01835-4

**Solution:** Fluid-based self-assembly with self-limiting interactions
aka
atomic layer deposition (ALD) in liquid phase

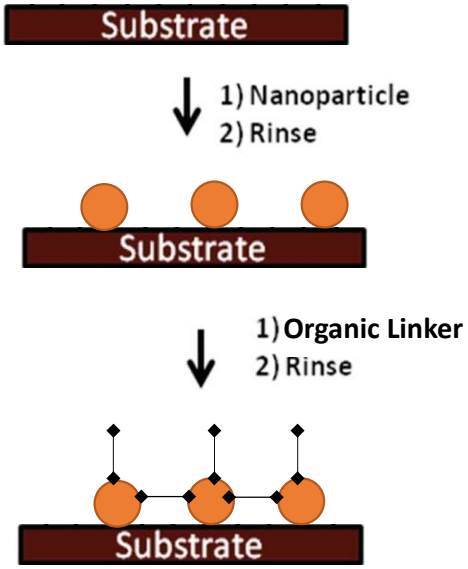


# Materials and their self-limiting Interactions

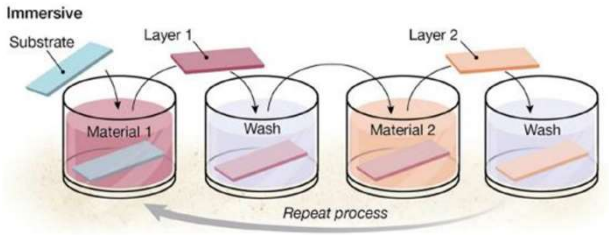
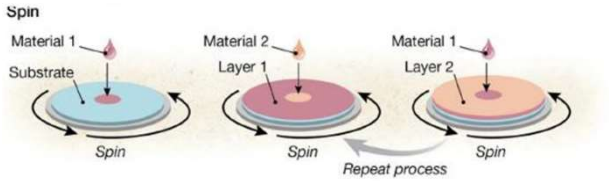
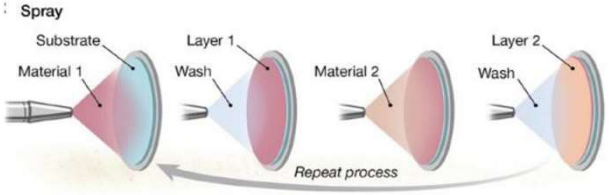
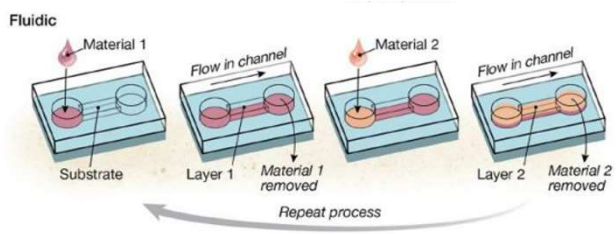
## Electrostatic Interactions




## Covalent Interactions

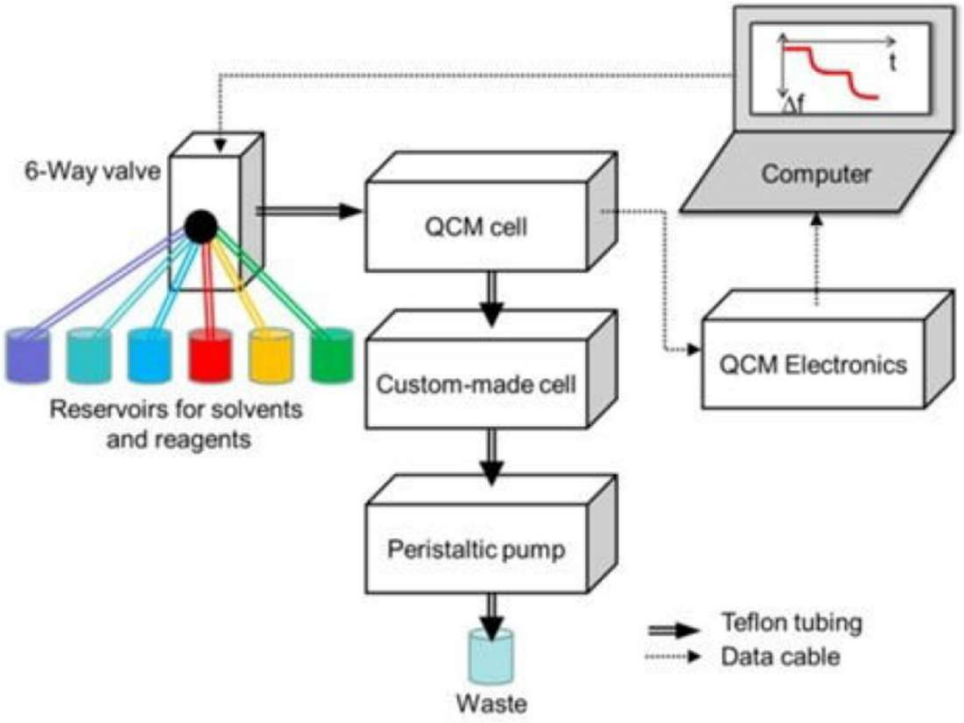


# Layer-by-layer- process options

| | pros | cons |
|---|---|---|
|  | ➢ Easy<br>➢ Interaction controls the deposition | ➢ Slow<br>➢ Rinsing needed<br>➢ High amount of material needed<br>➢ Whole substrate is coated |
|  | ➢ Fast<br>➢ Rinsing steps may be omitted<br>➢ Low amount of material needed<br>➢ Only one sided deposition | ➢ If interaction establishes only slowly → no layer formation<br>➢ Whole surface is covered |
|  | ➢ Fast<br>➢ Rinsing steps may be omitted<br>➢ Low amount of material needed<br>➢ Only one sided deposition | ➢ If interaction establishes only slowly → no layer formation<br>➢ Whole surface is covered<br>➢ Nozzle may clogg<br>➢ Inhomogenous layer formation |
|  | ➢ Interaction controls the deposition<br>➢ local deposition / Patterning<br>➢ Can be automated<br>➢ In-situ deposition control | ➢ Slow<br>➢ Microfluidic cell needed |

https://doi.org/10.3390/ijms19061641

# Microfluidic set-up

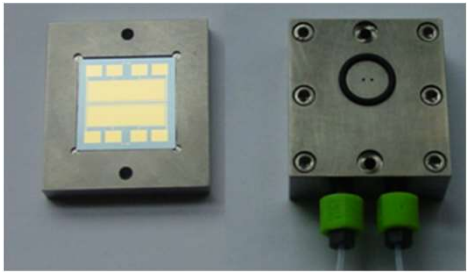



- Use of a commercial valve and pump
- Up to six materials or solvents for rinsing possible
- QCM-D for in-situ deposition control (may be omited)
- Computer control of pump, valve and QCM

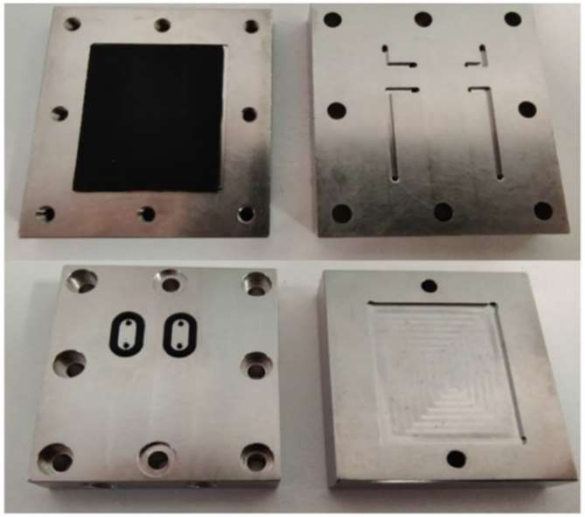
*Daskal et al: Langmuir* 2017, 33, 43, 11869–11877

# Microfluidic cells

- Use of a commercial QCM-D system
- ~1.2 cm coating area (circular)



- Custom made deposition cell for flat substrates
- Substrate materials : Si, glass, polymers, metal foils, paper etc.
- Variation of coating area possible, depending on cell
  - ~1.2 cm (circular)
  - ~0.6x1.6 cm(oval)
  - ~0.2x0.5 cm (oval)



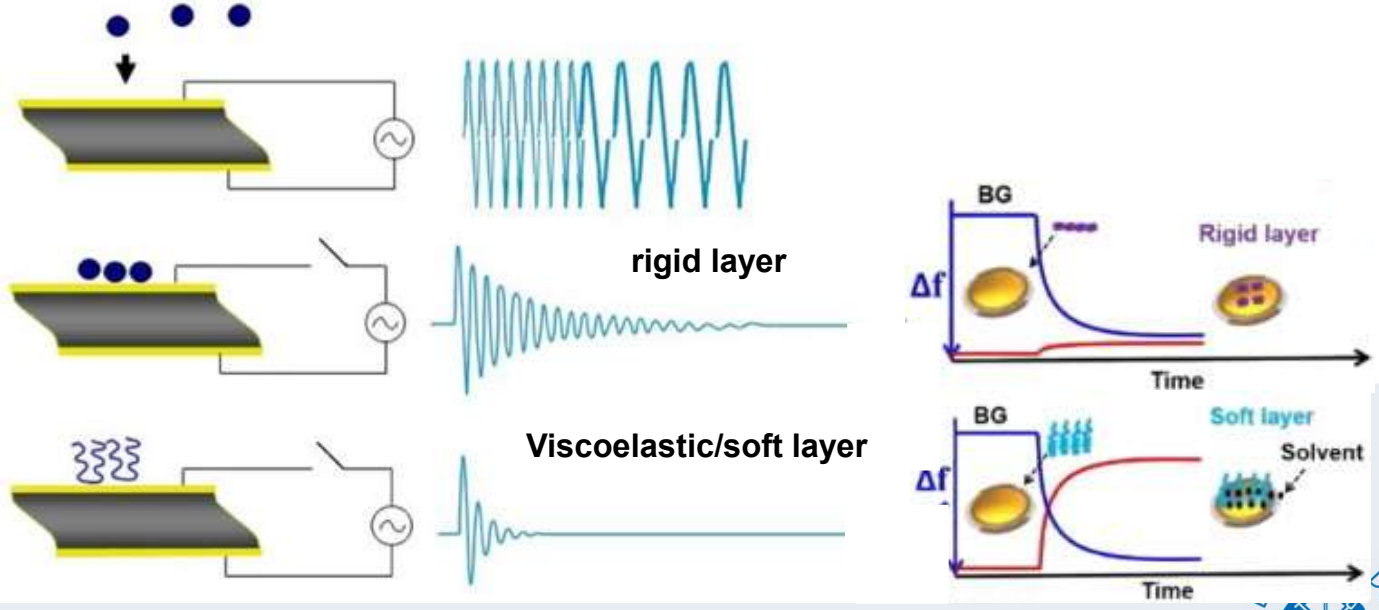
# QCM-D

Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D)

- is a high-resolution mass sensing technique
- observe and quantify molecular adsorption processes on a solid-liquid interface.
- Molecules or particles adsorbing on the sensor surface are causing a resonance frequency shift of the quartz crystal sensor (piezoelectric effect)
- In contrast to QCMs in vacuum, QCM-D can also gain information about the rigidity of an adsorbed layer via dissipation monitoring.

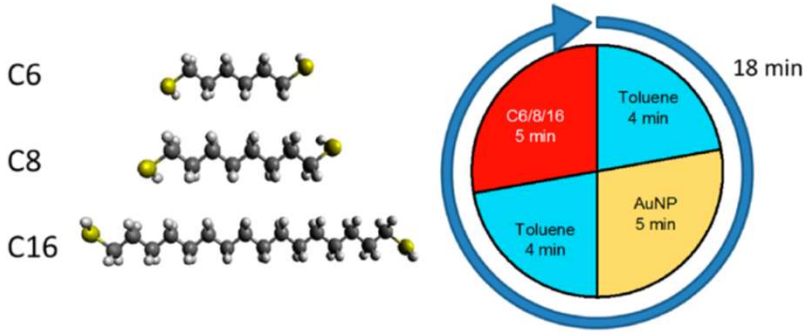
QCM in vacuum:

QCM-D in liquids:

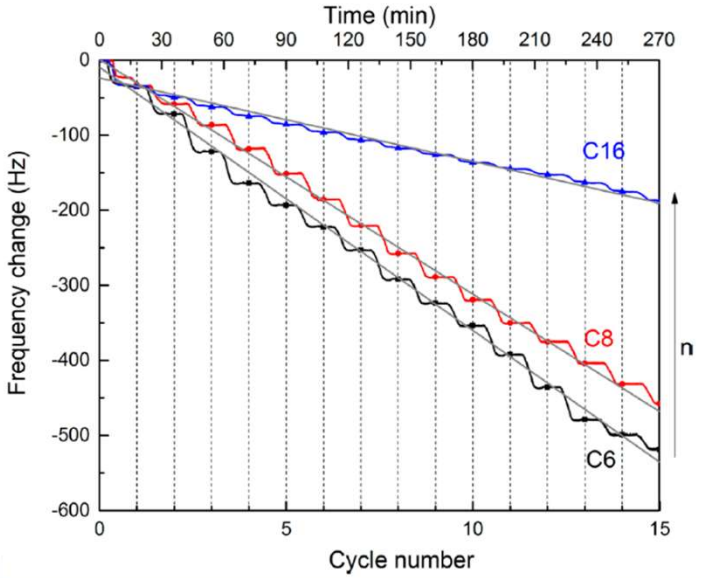


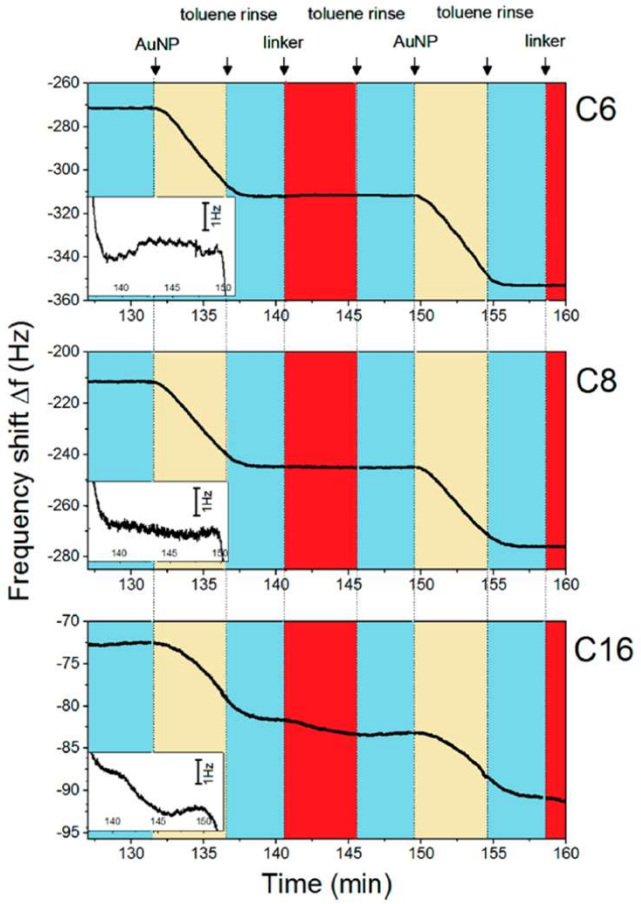

Sources: Biolin Scientific/Q-Sense & https://doi.org/10.1016/j.cis.2015.10.004

# Metal nanoparticle composites




➢ Application:
Chemiresistive Sensing



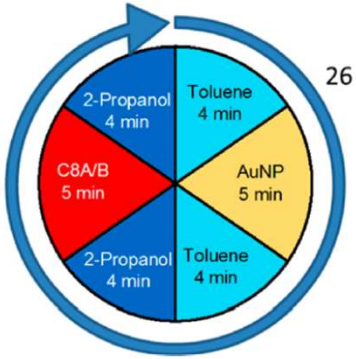


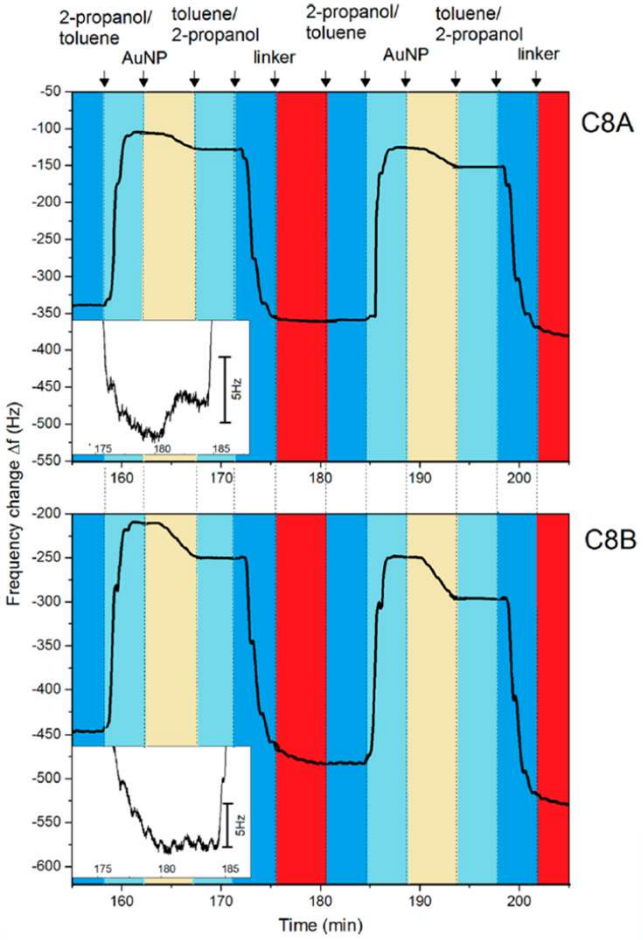

*Daskal et al: Langmuir* 2017, 33, 43, 11869–11877

# Metal nanoparticle composites

C8A

C8B

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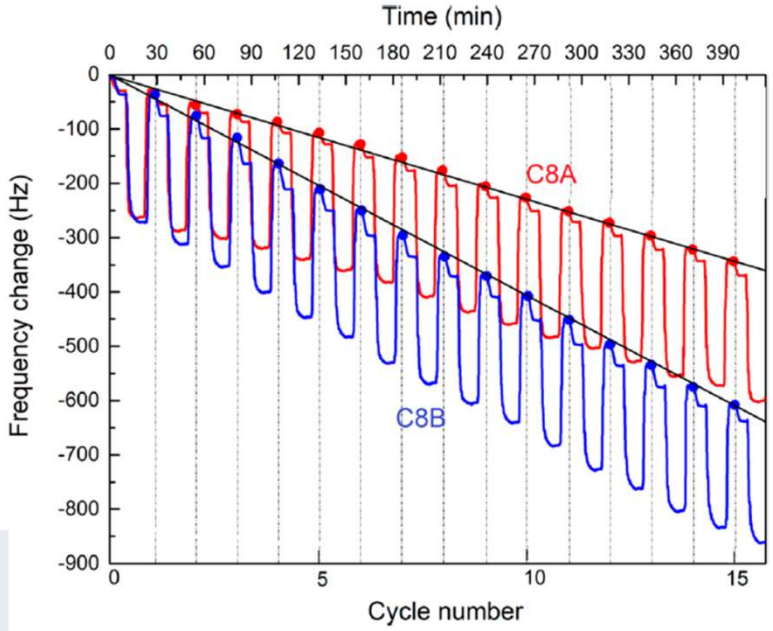
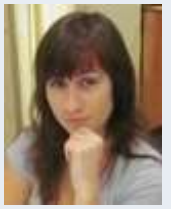
Chemiresistive Sensing

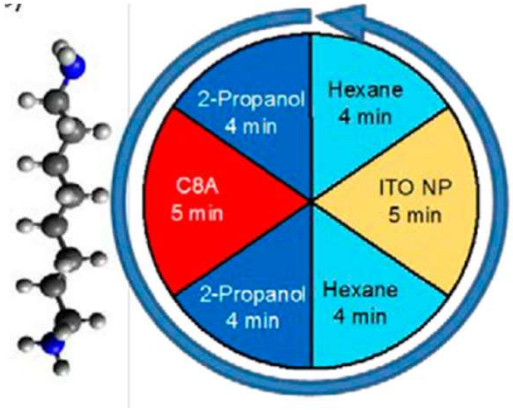


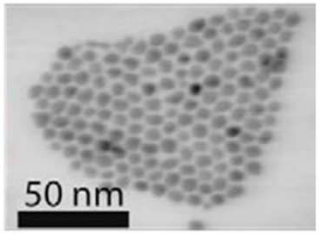


*Daskal et al: Langmuir* 2017, 33, 43, 11869–11877

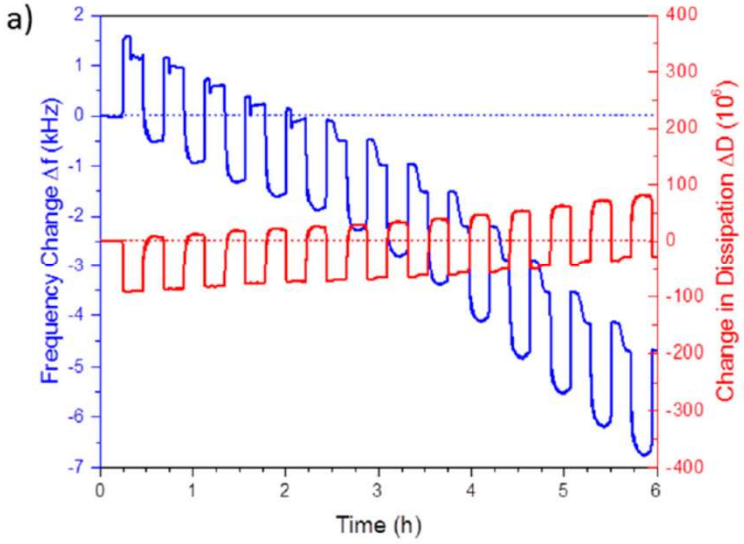
# ITO-Nanoparticle composites

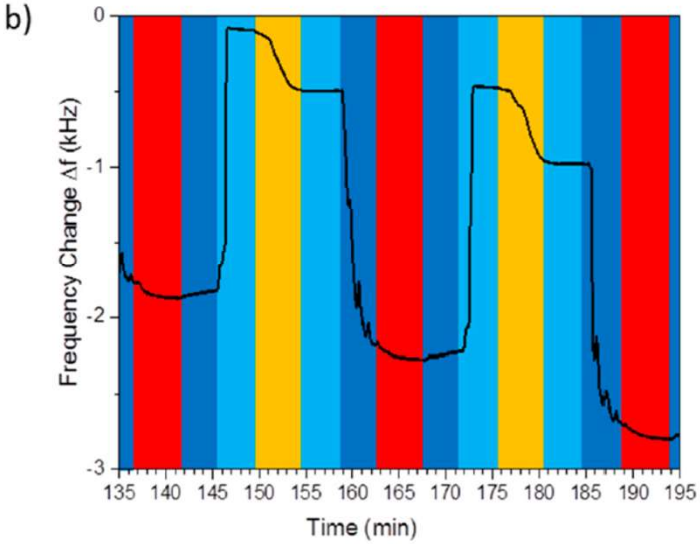



*in collaboration with Uni Tübingen*




- Application:
Chemiresistive Sensing





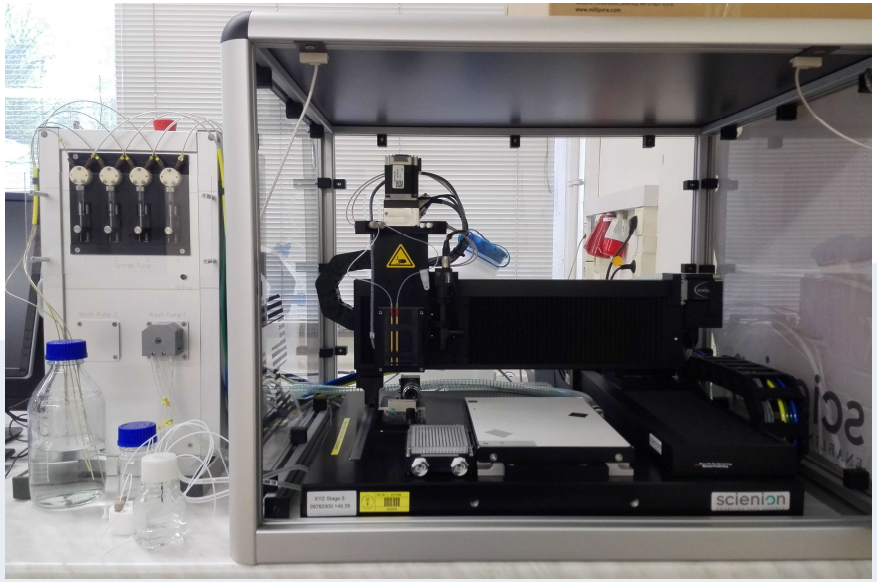

*Proceedings 2018, 2, 1516; doi:10.3390/proceedings2131516*

# Summary and Outlook

- Layer-by-layer self assembly is a powerful tool to prepare functional composite layers
- Many different composites can be prepared automatically

Current investigations:

- Integration of quantum dots → Investigation of optical properties
- Layer-by-layer dropcoating / Ink-jet printing → smaller coating areas



# Thank you!

Funding: