## MEng project CHESS-4: Adsorption of Nanoparticles at Surfaces

Detlef Smilgies (CHESS and CBE) and Tobias Hanrath (CBE)

The attachment of inorganic nanoparticles to surfaces is a fundamental problem underlying coating and printing techniques and also of paramount importance for electronic devices, such as solar cells and light-emitting diodes. The structure of the nanoparticle layer plays an important role in the device performance [Alivisatos].

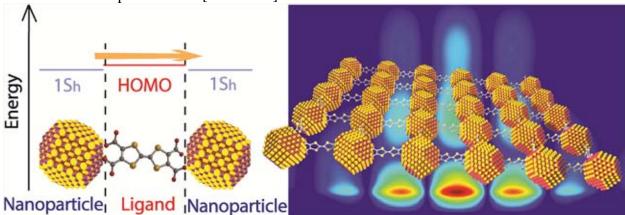


Figure 1: Ordered PbS nanoparticle array with bifunctional linker on a wafer surface forming a field-effect transistor [Alivisatos].

There are multiple facets to the adsorption of soft materials to surfaces: first of all there is the van-der-Waals attraction between nanoparticles and the substrate which can be understood within the Hamaker model. Then there is the surface energy of the silica substrate (i.e. silicon wafers covered with native oxide, glass slides, silica-coated quartz oscillators) which can be modified using self-assembled monolayers [Willner]. These can be either neutral, such as octodecyl trichlorosilane (OTS), or functional such as aminopropyl triethoxysilane (APTES) or phenyl trichlorosilane (PTS). We would like to characterize the Langmuir isotherms and the adsorption kinetics [Abruna]. Goal would be to prepare monolayer and sub-monolayer systems in equilibrium with the solution phase in a controlled way.

We will use quartz-crystal mass spectroscopy [Barron, Johannsmann] and dissipation (QCM-D) using a recently acquired Biolin Q-Sense instrument, which also permits to control the substrate temperature. A pilot study showed that iron oxide particles of about 10nm diameter absorb well at room temperature in equilibrium with the solution. We would like to obtain more detailed information, how the adsorption depends on the particle size. It would also be very interesting to find out, at what temperature nanoparticles desorb as a function of their size and determine their binding energy.

We will complement these measurements with grazing-incidence x-ray scattering at CHESS D1 beamline to characterize the adsorption, conformation, and self-assembly of nanoparticles on clean or modified silicon oxide surfaces. The project student will be invited to participate in the x-ray characterization of his/her samples in the upcoming beamtime at CHESS.

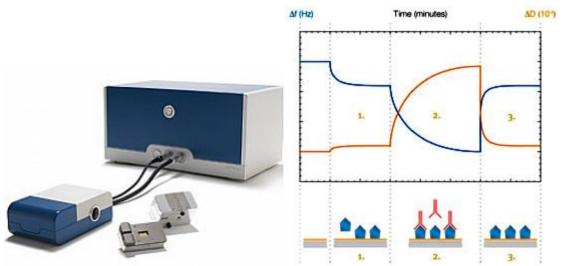


Figure 2: Q-Sense QCM-D system with sensor and controller (left). Typical QCM-D scan: 1. absorption of a linker molecule, 2. absorption of an elongated molecule, 3. rinsing and removal of elongated molecule. Note the shifts in frequency related to the mass uptake and in dissipation related to the interaction of attached molecules with the liquid.

Suggested reading

[Alivisatos] Scheele et al.: "PbS Nanoparticles Capped with

Tetrathiafulvalenetetracarboxylate: Utilizing Energy Level Alignment for Efficient Carrier Transport", ACS Nano 8, 2532–2540 (2014).

[Abruna] David Acevedo, Richard L. Bretz, Jorge D. Tirado, and Hector D. Abruna: "Thermodynamics of Adsorption of Redox-Active Self-Assembling Monolayers of Transition-Metal Complexes", Langmuir 1994,10, 1300-1305; Jorge D. Tirado, David Acevedo, Richard L. Bretz, and Hector D. Abruna: "Adsorption Dynamics of Electroactive Self-Assembling Molecules", Langmuir 1994, 10, 1971-1979.

[Barron] Daniel Garcia-Rojas and Andrew R. Barron: "Nanoparticle deposition studies using a quartz-crystal microbalance", <u>http://cnx.org/content/m46155/1.2/</u>.

[Johannsmann] Diethelm Johannsmann: "The Quartz Crystal Microbalance in Soft Matter Research" (Springer, Heidelberg, 2015), available as electronic book from the Cornell library: http://link.springer.com.proxy.library.cornell.edu/book/10.1007%2F978-3-319-07836-6

[Willner] Shipway et al.: "Nanoparticle Arrays on Surfaces for Electronic, Optical, and Sensor Applications", ChemPhysChem 1, 18-52 (2000).