Overview

QCM-D studies of engineered nanoparticles

Engineered nanoparticles are increasingly used in various applications such as sorbents, optical or electronic materials, filler materials, and drug carriers. Both physical and chemical properties of nanoparticles may be different compared to bulk materials, and such size-dependent effects are usually stronger the smaller the particles are. Not only is it of interest to tweak and optimize the nano-material functionality, but it is also of utmost importance to avoid potential adverse effects of nanoparticles for human health and the environment.

QCM-D offers a unique way of studying nanoparticle interactions both in liquid and gas phase. In this overview we present three examples of nanoparticle characterization with QCM-D.

I. Aggregation and deposition kinetics

The rate of mass change and the rate of rigidity change versus time plots are useful indicators of particle behavior during deposition on surfaces. Nanoparticle interactions with solid surfaces are of interest to learn about nanoparticle surface affinity, e.g. for filtering/removal of nanoparticles from water or air, for collecting samples for later characterization, or for preventing nanoparticle induced fouling. Lipid membranes on QCM-D sensors can be used as biomimetic model systems to study nanoparticle-cell membrane interactions, and are of interest both for nanodrug screening and for nanoparticle toxicity screening. An important aspect of nanoparticle interactions is also to learn about nanoparticle agglomeration.

Particle deposition – or absence of deposition - onto a surface can often be rationalized by an electrostatic reasoning. In **Figure 1** it is shown how the deposition rate of fullerene nanoparticles onto a sili-

ca-coated sensor increases with increasing electrolyte concentration (1, 10, and 30 mM NaCl at pH 5.2), leading to decreased charge repulsion between the particle and the surface [1]. A higher deposition rate was obtained by coating the silica surface with positively charged poly-L-lysine (PLL) (curve with the highest slope).

The characterization of nanoparticles, e.g. industrial nanoparticles, is important to optimize function and production quality. As an example the adsorption of Ludox™ silica particles to polymer (PDADMAC)-coated surfaces is studied by QCM-D [2]. The dissipation data for such measurements, see **Figure 2**, shows significant changes both with particle concentration and with experiment time. The changes over time at a concentration of 1015 Ludox™ particles/L suggest that a significant degree of surface reorganization occurs at this particle concentration, as opposed to at lower and higher concentrations. A suggested reorganization scenario is illustrated in the graph.
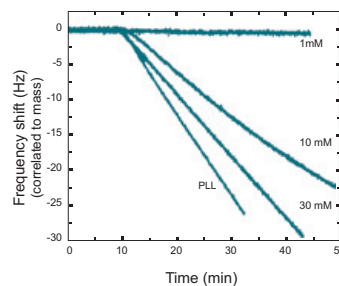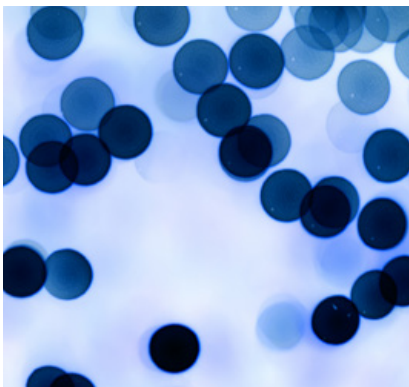
Figure 1: Deposition rate of fullerene nanoparticles onto silica measured with QCM-D.
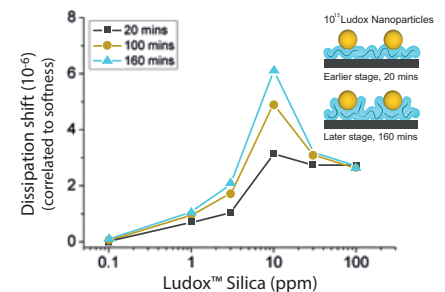

Figure 2: Adsorption of Ludox silica particles to polymer coated surfaces studied by QCM-D.

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Example: QCM-D studies of nanoparticles in the environment

A growing field of nanoparticle research relates to the characterization of emissions into and fate of nanoparticles in the environment, where exposure scenarios are commonly formulated using life cycle-based methods. Quantification of nanoparticles in actual environmental samples is one prerequisite for better understanding of exposure and effects of nanoparticles, as well as model studies on nanoparticle behavior and transformations under environmentally relevant conditions.

For example, CeO_2 nanoparticle deposition has been studied using sensors coated separately with the environmentally relevant minerals silica, iron oxide, and alumina which can be applied to examine the importance of these mineral phases on nanoparticle deposition [3]. The rate of frequency and dissipation shifts followed the order: silica > iron oxide > alumina in 10 mM NaCl at pH 4.0. The kinetics was qualitatively consistent with the predictions based on classical colloidal stability theory. Further studies in the presence of low levels of organic matter implied electrosteric effects.
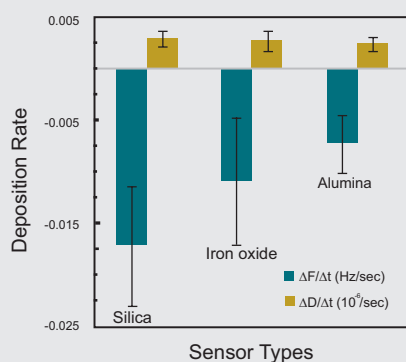
Figure 3: Deposition rate of CeO_2 nanoparticles onto different materials.

II. Build-up of surface-confined nanocomposite structures

Surface-based analytical methods offer advantages with respect to analysis and characterization of the sequential build-up of nanostructured layers in a controlled way. Examples of nanocomposite structures, which have been studied by QCM-D, include, e.g., graphene-based layer-by-layer structures and assemblies of inorganic nanoparticles and cellulose nanofibres. In the example shown in **Figure 4**, a layer-by-layer approach was employed for constructing colloidal semiconductor quantum dots (QDots) and polyelectrolyte peptides in nanocomposite structures that facilitate non-radiative Förster-type resonance energy transfer (FRET) [4]. The build-up of these layers was monitored by QCM-D. The ability to control photoluminescence decay lifetime was demonstrated by proteolytic enzyme activity, opening up new possibilities for biosensor applications.

Intact peptide film assembly of QDots

After protease attack
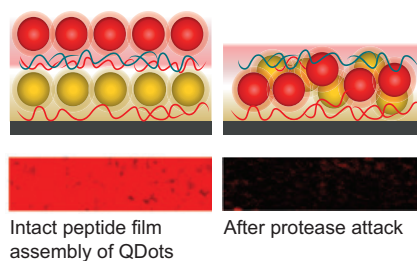
Figure 4: Layer-by-layer structure of quantum dots and polyelectrolyte peptides before and after protease attack.

III. Characterization of associated solvent

The acoustically coupled mass measured by QCM-D includes coupled water. For nanoparticles adsorbed to a surface, the amount of water associated with a particular particle (or biomolecules such as globular proteins) is dependent on the particle coverage and how the particle is linked to the support [5, 6]. With increasing nanoparticle coverage the trapped solvent coat (upper part in **Figure 5**) of adjacent nanoparticles overlaps, and the measured average amount of water per nanoparticle decreases (lower part of **Figure 5**). Moreover, the dissipation can provide unique information about the mechanical properties of the contact zone between nanoparticles and the surface on which they are attached.

Adsorbed nanoparticle

Trapped solvent coat

Increasing coverage
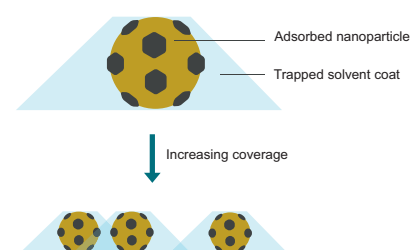
Figure 5: Illustration of trapped solvent coat on nanoparticles. Higher nanoparticle coverage decreases amount of solvent per particle.

References:
[1] Chen KL and Elimelech M, Aggregation and Deposition Kinetics of Fullerene (C60) Nanoparticles, Langmuir, 2006, 22 (26), 10994–11001.

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[3] Liu X, Chen G, Su C, Influence of Collector Surface Composition and Water Chemistry on the Deposition of Cerium Dioxide Nanoparticles Environ. Sci. Technol., 2012, 46 (12), 6681–6688.

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[6] Johannsmann D., Reviakine I., Richter R.P. Dissipation in films of adsorbed nanospheres studied by quartz crystal microbalance (QCM) Anal. Chem. 2009, 81, 8167-8176.

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