

Visualization of dynamic changes and the effects of coatings on silver nanoparticles by Surface Enhanced Raman Spectroscopy

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A wide variety of applications for engineered nanoparticles leads to increasing emissions into the environment. After entering the aquatic or terrestrial compartment, nanoparticles likely undergo changes caused by weathering or interactions with dissolved substances forming coatings on the particles. Hence, the surface properties will no longer be characterized by the nanoparticle itself, but rather by the properties of the coating material. Stability and transport properties particles will be altered significantly by different coating materials.

Knowledge of the development and stability of coatings is therefore crucial to predict the fate of nanoparticles in the environment. Surface enhanced Raman Spectroscopy (SERS) is a spectroscopic technique, which makes use of the signal enhancement caused by surface plasmon resonance and chemical enhancement typically found at silver nanoparticles and other nanostructured metals (e.g. Au, Cu). Thus the signal of the molecules adsorbed to the nanoparticles will be enhanced significantly and dynamic changes of the materials adsorbed to the particles can be studied. SERS is rather insensitive to dissolved molecules since the electromagnetic SERS enhancement strongly decreases with growing distance ($\sim d^{-12}$). The technique works with little sample preparation and sample volumes suitable for microfluidic experiments and environmental samples.

Citrate reduced and stabilized as well as hydroxyl-ammoniumchloride reduced silver nanoparticles were coated with humic acid, seaweed extract, and polygalacturonic acid. After adding the coating materials, the suspensions were centrifuged to remove excess coating materials. Changes of the pH-value of the solution and an exchange of the coating material were done to study the stability of the coating. Here, Raman spectroscopy gives direct access to the protonation of humic acid on the surface which immediately effects the spectrum.

The characterized nanoparticles were then brought into contact with physically and chemically heterogeneous surfaces to investigate the attachment coefficients and potential blocking. Chemical mapping using Raman microspectroscopy and SERS not only gives access to the spatial distribution of the nanoparticles but also to the chemical environment around the nanoparticles.

Water H₂¹⁸O isotope studies in the AIDA cloud simulation chamber

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Isotopic studies can provide additional information on cloud physics, which have a significant impact on global climate. The conventional isotope-selective measurement technique, Isotope Ratio Mass Spectrometry (IRMS) is however not adapted to study dynamic processes such as cloud formation. Laser based measurement techniques offer both high precision and a fast response to follow the cloud formation process in real time. In the recent ISOCLOUD campaign at the AIDA cloud and aerosol chamber, different laser-based instruments were used to jointly obtain information about isotope ratio changes in both the water vapor and ice phases during simulated cloud formation processes. Here we report on two instruments used to quantify the H₂¹⁸O/H₂¹⁶O ratio. One of the instruments, ISO-APiCT (PTB/KIT), an open path spectrometer based on tunable diode laser absorption spectroscopy (TDLAS) measures the isotopic ratio of the vapor phase. Open-path TDLAS has been successfully applied to in-cloud studies on H₂¹⁶O [2]. The second instrument based on Optical Feedback Cavity Enhanced Absorption Spectroscopy (OF-CEAS, Grenoble/KIT) extractively samples either total water or, if connected behind a pumped counterflow virtual impactor, the ice phase only. The OF-CEAS technique has already been used in different water isotope studies, including airborne studies [3]. We show a characterization of both instruments, including their time response to sudden isotope ratio changes, as well as preliminary results obtained during ice cloud formation.

[1] Krämer M. *et al.*, *Atmos. Chem. Phys.* **9**, 3505-22 (2009).

[2] Gurlit, W. *et al.*, *Applied Optics* **44**, 91-102 (2005) [3]

Iannone R.Q. *et al.*, *J. Geophys. Res.* **115**, D10111 (2010) ;
Isot. Env. Health Stud. **45**, 303-20 (2009)