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Investigation of Surface Coatings on Silver Nanoparticles by Surface Enhanced Raman Spectroscopy

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The behavior of engineered inorganic nanoparticles (EINP) in the environment is strongly affected by their surface properties. Once introduced in the aquatic or terrestric environment, the nanoparticle surface may be altered by weathering or the formation of a coating. These changes influence the interactions of the nanoparticle with natural surfaces or interfaces as well as with other particles. Natural organic matter for example is known to have a stabilizing effect on most nanoparticles. Therefore the assessment of the fate and transport of nanoparticles in the environment requires a precise knowledge of the influence of the coating and its modifications under natural conditions.

A suitable tool for the investigation of coatings on silver nanoparticles is surface enhanced Raman spectroscopy (SERS). Although silver nanoparticles themselves do not have a distinct Raman signal, the Raman signal of adsorbed or nearby substances is enhanced by a factor of 10^3 - 10^6. This leads to a considerably higher sensitivity of SERS in comparison to normal Raman microscopy. Therefore, coatings on silver nanoparticles should be accessible via the SERS effect. As a first step, plain and citrate stabilized silver nanoparticles were mixed with different natural coating substances (polygalacturonic acid, seaweed extract, and humic substances) and filtered with a polycarbonate filter to remove excessive coating material. Afterwards, the nanoparticles were redispersed from the filter by ultrasonification. This washing procedure was repeated three times while always maintaining the same concentration of nanoparticles. SERS spectra were recorded after each washing step with a LabRAM HR Raman mircospectrometer (Horiba Scientific, Japan, $\lambda = 633$ nm, 20x water-immersion-objective, measurement time 10 s).

First results indicate the formation of a stabilizing layer around the nanoparticles after contact with humic substances, thus providing experimental evidence to the stabilization of EINP by humic substances on a μm level. At low concentrations of dissolved humic substances, a specific SERS signal is only observed for coating materials adsorbed to silver nanoparticles. This renders the method less sensitive to dissolved potential coating substances. Furthermore, additional bands of coating which appear in the SERS spectra due to chemical enhancement (charge transfer) indicate an interaction of the used coating material with the nanoparticle. However, there is an ambiguity between coatings on the nanoparticles and dissolved macromolecules in the close vicinity of (but not attached to) nanoparticles which has to be resolved.