

Structural assessment of self-assembled cationic monolayers on gold nanopillars in the presence of nitrate through surface enhanced Raman spectroscopy

Timo Küster & Geoffrey D. Bothun

University of Rhode Island

Detection of anionic seawater nutrient pollutants is essential to understand and prevent harmful algae blooms and maintain water quality. Current on-site methods for nutrient detection often require extensive sample preparation, are limited by interfering ions and molecules, and have detection limits above concentration thresholds required for detection under nutrient limited conditions, in which a small variation of concentration can lead to sudden growth events, such as algae blooms.

Surface Enhanced Raman Spectroscopy (SERS) is a method utilizing the enhancement of otherwise weak Raman scattering in the presence of nanostructured metal surfaces where analytes are within approximately 2 nm of the surface. The energy shifts in photons scattered by the target analyte are specific to its structure and can even be used to identify the conformational state of target molecules. To reduce the distance between the analyte molecules and substrate, samples are often dried out on two dimensional SERS substrates. For *in situ* measurements in an aqueous phase, pre-concentration methods relying on surface functionalization with ligands can be used to increase the total number of target molecules within the SERS active region.

Cationic self-assembled cysteamine monolayers (catSAM) have been successfully utilized for the direct, continuous *in situ* detection of nitrate and phosphate anions at micromolar concentrations. We show an “on/off switching behavior” triggered by changes in solution pH, likely caused by activation of the catSAM amino head groups. In this work we focus on a thorough investigation of the underlying interaction mechanisms. The pre-concentration mechanism and specificity was analyzed by varying environmental parameters such as pH, anion species, and concentration and extensive peak assignments, providing insight to the analyte/catSAM interaction mechanisms. Our findings will enable better informed design parameters for a continuous *in situ* nutrient detection measurement platform in seawater, actively supporting nutrient detection and mitigation efforts in the marine environment.