Surface enhanced Raman spectroscopy of organic molecules on magnetite (Fe_3O_4) nanoparticles

NAMHEY LEE[1], P. JAMES SHUCK[2], PETER S. NICO[1] AND BENJAMIN GILBERT[1]

[1]Earth Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States
[2]Molecular Foundry, Lawrecne Berkeley National Laboratory, Berkeley, CA 94720, United States

The adsorption configuration of organic molecules on mineral surfaces is of great interest as it can provide an important insight for both engineered and natural systems. Surface enhanced Raman spectroscopy (SERS) is a highly surface sensitive approach for obtaining Raman data from molecular speices adsorbed to SERS-active substrates. In conventional SERS, the Raman signal at a metallic surface is amplified by the excitation of surface plasmon resonances and local enhancement of the electromagnetic field. For a small subset of organic molecules that bind strongly to semiconductor surfaces, formation of an interfacial charge-transfer complex can cause high chemical enhancement of the Raman signal. Yet, so far, chemical SERS involving non-mentallic substrate is largely limited to enediol family molecules. Many fields of interfacial chemistry thus lack a class of SERS-active substrates that possess representative surface structure and chemistry that are not limited to a narrow range of sorbate characteristics.

Here we show by comparing Raman on non-conductive maghemite versus mangetite, a conducting mixed valence iron oxide, that mangnetite can act as a SERS substrate capable of electromagnetically enhancing the Raman signal for diverse surface sorbed organic molecules [1]. Our study demonstrates that magnetite (Fe_3O_4) nanoparticles provide a SERS signal via an electric field enhancement from oxalic acid and cysteine sorbed on magnetite surface with different functional groups. In fact, our data suggests a new geometry for cysteine binding on oxide surface. Currently, we are investigating the use of this approach for inorganic, oxyanions sorbents including aresenate.

Magnetite nanoparticle combines benefits from both metal-based and chemical SERS by providing an oxide surface for studies of environmentally and catalytically relevant detailed chemical bonding information. The discovery of magnetite-based SERS substantially extends the scope for the study of interfacial adsorption reactions at metal oxide interface.

[1] Lee *et al*. (2015) *J. Phys.l Chem. Letters* **6**, 970-974.