Monitoring the Aggregation of Particles through Raman Spectroscopy

Introduction

Raman spectroscopy is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. Raman spectra are obtained by irradiating a sample with a powerful laser source of visible or infrared monochromatic radiation. Photons from the laser are scattered by the sample inelastically, exchanging energy with the sample based on molecular vibrational modes in the molecule. The energy exchange causes the Raman scattered photons to be shifted in energy (and therefore in wavelength). The difference in energy between the incoming photon and the scattered photon is characteristic of the vibrational modes of the molecule, which gives us useful information about the structures of chemical compounds. This vibrational information includes both functional group identification and the so-called “fingerprint” region, similar (but not identical) to the information provided by FTIR techniques.

Zeta potential, which is also known as electrokinetic potential, is a measure of the surface charges of the nanoparticles – the magnitude of electrostatic and charge repulsion or attraction between nanoparticles. The measurement of zeta potential gives great details regarding the causes of aggregation of nanoparticle samples.

Raman scattering can also occur in solids, in which case the low-energy phonon modes provide information about particle size and shape as well as the mineral phase. This suggests that Raman spectroscopy can provide useful information about the composition and structure of metal oxide nanomaterials, such as ZnO, TiO_2, as well as carbon-based engineered nanomaterials such as graphene, carbon nanotubes, and fullerenes. The possible environmental impact of these materials is of increasing interest from both a scientific and a social viewpoint. In-depth investigation of how these materials interact with the environment is currently difficult because existing methods for detecting and quantifying them are limited: electron microscopy is slow, and atomic spectroscopy does not provide adequate detail.

Objective

The ultimate objective of the current research is to develop a practical method for routine detection of metal oxide nanomaterials in environmental water samples. Previous research supported by this same funding opportunity (Chris Fowler, 2010-2011) provided data that proves that Raman spectroscopy can be usefully applied to this problem.

replicate samples.

Two improved methods for preparing the samples have been identified: collect nanoparticles from a larger volume of water sample by filtration through a nanoporous membrane, or collect Raman spectra of the liquid samples directly. The succes so that the Raman signal is lost. We will solve this problem by focusing the laser beam just inside the plastic cuvette holding the sample, using a linear translation stage to achieve precise control over the position of the cuvette and the laser probe. This will allow us to collect Raman spectra from liquid samples, which is needed to understand how measurements of particle size and aggregation correlate with Raman spectral quality.

We intend to work with commercially available suspensions of TiO2 (anatase & rutile) and ZnO nanoparticles. The nominal size range for these particles is 40 to 60 nm, but we want to confirm this by electron microscopy in the facilities of the Center for Manufacturing Research. This will also let us see the particle shape and how the particles fit together into aggregates.

The second technique to characterize the samples is by particle size determination, which will determine the size of both individual particles and aggregates. The aggregated particles in a water sample are a mixture of both individual particles and aggregates of different sizes. The Malvern Zetasizer instrument, available through collaboration with Dr. Holly Stretz (Chemical Engineering) will give us quantitative data on the extent of aggregation. We will prepare samples of all three types of particles (rutile, anatase and zinc oxide) at several different pH levels (e.g., pH 4, 6, 8) and with different concentrations of a non-reactive salt such as sodium nitrate. We will meas correlate that with the intensity of Raman signal collected from the liquid suspensions. Once we know the preferred conditions (pH & ionic strength) for the best possible Raman spectra of suspended or filtered particles, we will prepare samples containing mixtures of different types of nanomaterials and collect Raman spectra of these mixtures. We will use multivariate statistical techniques such as partial least-squares regression (already developed in earlier work) to build a calibration model that allows us to identify the composition of unknown samples.

Previous Research Experience

Student Research Grant

Budget Form

Student name: Yanxiao Ma

Proposal title: Monitoring the Aggregation of Particles through Raman Spectroscopy

Amount requested: $750.00

Itemize as specific as possible below:

$200.00 – reagent and consumable for Malvern Zetasizer;

$150.00 – commercially available nanoparticles;

$250.00 – a translation stage to position the cuvettes of Raman spectroscopy;

$150.00 – fiber optic probe holder for Raman spectroscopy.