Monitoring the Aggregation of Particles through Raman Spectroscopy

Name: Yanxiao Ma

Advisor: Dr. Andrew Callender

Submission Date: 19 Oct. 2012

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. However, the previous method suffered from difficulties with sample preparation. Specifically, that method involves drying out small volumes of water sample (200 μL) in the wells of a plastic microplate, then collecting Raman spectra of the small quantity of solids that remain (< 1 mg). This method is slow and shows an undesirable level of variance in

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 success of both methods strongly depends on our ability to control the aggregation of these particles in the samples. (The filtration approach would benefit from aggregation, but aggregation is undesirable in spectroscopy of liquid samples because it makes the sample opaque.) Aggregation depends on the particle size and surface charge (zeta potential). The surface charge depends in part on the pH and ionic strength of the water sample. Thus, samples with different pH or salinity levels might give significantly different results for the nanoparticle analysis. Our immediate goal for this research is to measure the aggregation as a function of pH and ionic strength, so that we can understand how to control aggregation as we prepare samples.

Methodology

Since the purpose of this research is to be able to collect the best possible Raman spectra of these materials, the first piece of the research will be to investigate better ways to collect Raman spectra of liquid suspensions of particles. Previous efforts to do so failed because the aggregated particles scatter all kinds of light (they appear milky white),

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 measure the particle size distribution and

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

During my undergraduate studies, I have attended an instrumental analysis course. I have practically carried out experiments using Raman spectroscopy, atomic and molecular spectroscopy, IR, UV, NMR etc. In the course, I was given an opportunity to design my own experiment to determine the structure of ethyl benzoate using Raman spectroscopy, NMR, and IR spectroscopy. On top of that, in the time of my final year undergraduate research about The Crystallization of PEO Network, I have mastered the Origin, AutoCAD and Labview software. Therefore, I am confident that I can manage the project competently.

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.