Silica sol-gels containing calcein blue as surface-enhanced Raman spectroscopy (SERS) sensors for metal ions

Evan R Carlson; Dr. Elizabeth J. O. Atkinson

Department of Chemistry, Linfield College, McMinnville, Oregon 97128

Introduction

Surface-enhanced Raman spectroscopy (SERS) is a spectroscopic technique which relies on the inelastic scattering of photons from a target molecule. SERS is both sensitive and specific; the technique produces a unique spectrum for all molecules while offering up to single molecule detection with proper conditions. However, acquisition of SERS spectra requires the presence of a suitable substrate, such as noble metal nanoparticles or roughened metal electrodes.

Silica sol-gels are porous, amorphous silica matrices formed by the hydrolysis of a silicon containing precursor molecule. As a result of their unique structure, these compounds have a variety of unique properties, such as high surface area and low thermal conductivity. They can be easily modified, and metal-colloid-modified silica sol-gels represent a relatively unknown class of compounds which can function as substrates for SERS measurements. In this study, the fluorescent dye calcein blue (CB) was chosen as a target molecule due to its ability to interact with various metal ions. As a result, it has found use as an indicator in EDTA titrations and has potential applications in metal ion sensing devices. Thus, detection of calcein blue within modified sol-gels could lead to the development of new techniques for the detection of metal ions. Such techniques could have applications in fields such as water quality analysis or other environmental assays.

Materials and methods

Materials: Concentrated ammonium hydroxide was purchased from Pharmco-AAPER. All other reagents were purchased from Sigma-Aldrich and were used as received. Deionized water was used throughout the study.

Methods: Gels were prepared by the base-catalyzed hydrolysis of tetramethyl orthosilicate (TMOS). Methanol (2.26 mL), deionized water (0.762 mL), and ammonium hydroxide (0.0026 mL, 30%), were combined in a beaker and added to a second beaker containing TMOS (1.92 mL) and methanol (2.26 mL). The mixture was stirred 25 minutes and silver colloid (7.00mL), prepared following modification of the Lee and Meisel citrate reduction method, was added. The mixture was stirred an additional 25 minutes, and water (0.5 mL) or calcein blue (0.5 mL, 5.6 mM) added. The mixture was stirred three minutes and poured into cuvettes then covered and allowed to age 24 hours. Aged gels not containing calcein blue were placed in vials containing calcein blue (5.6 mM) for at least 48 hours prior to SERS spectrum acquisition. Gels were washed with ethanol followed by acetone prior to supercritical drying.

Instrumentation: SERS measurements were obtained using a custom Raman spectrometer having a 532 nm excitation beam and thermoelectrically cooled CCD. Supercritical drying was performed using Samdri-795 critical point dryer.

Results

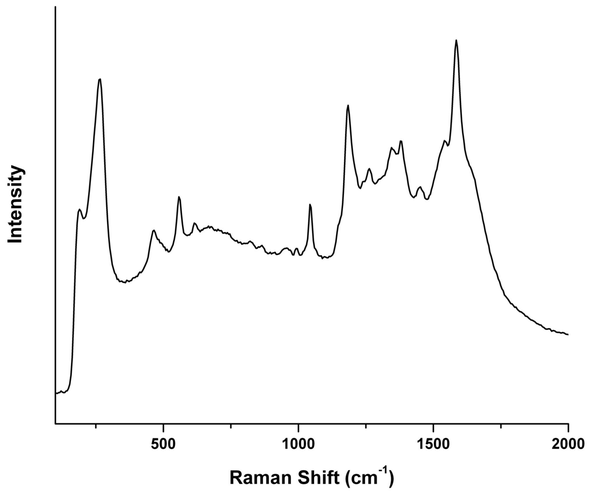

Figure 1: SERS spectrum of calcein blue solution (5.6 mM) combined with silver colloid in the presence of Na_2SO_4 aggregating agent.

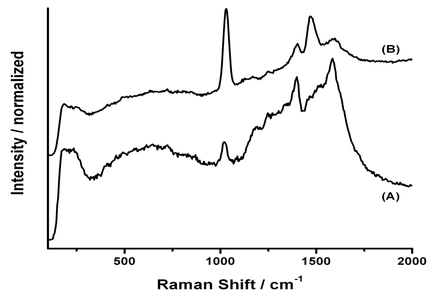

Figure 2: SERS spectra of A) a silica sol-gel containing silver colloid after 48 hour CB solution soak, and B) a silica sol-gel containing only silver colloid.

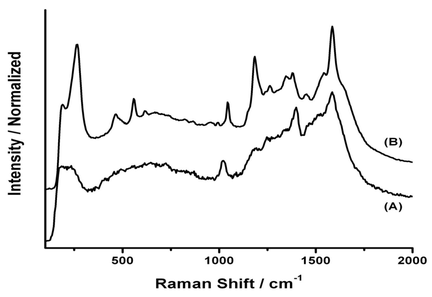

Figure 3: SERS spectra of a) a silica sol-gel containing silver colloid after 48 hour CB solution soak, and b) CB solution (5.6 mM) combined with silver colloid in the presence of Na_2SO_4.

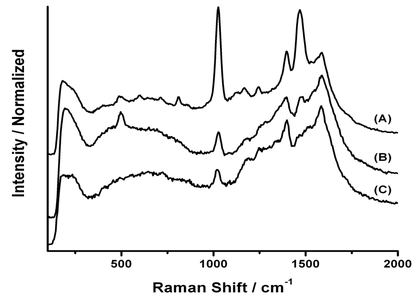

Figure 4: SERS spectra of A) a sol-gel containing silver colloid and calcein blue, B) the same gel after washing with UPDI water, and C) a sol-gel containing silver colloid after soaking in aqueous CB solution.

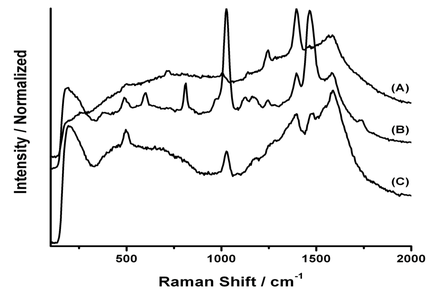

Figure 5: SERS spectra of A) an aerogel containing silver colloid and CB dried after washing with ethanol and acetone, B) the same gel prior to being dried or washed, and C) a sol-gel containing silver colloid after soaking in aqueous CB solution.

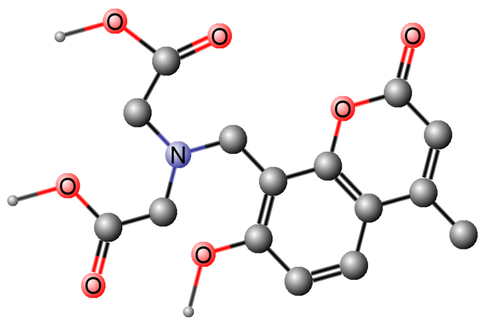

Figure 6: Molecular structure of calcein blue.

Conclusions

As indicated by figures 2 and 3, a SERS spectrum of calcein blue was successfully obtained from a modified silica sol-gel substrate after CB solution was allowed to diffuse into the gel pores for an extended period of time. We can thus conclude that sol-gels containing silver nanoparticles are viable substrates for the SERS of calcein blue, and that these materials could be useful in sensing applications. Further, sol-gel sensing materials can be made by inclusion of calcein blue in the initial reaction mixture, as shown by the spectrum in figure 4a and 4b. While it is hoped that this method offers greater stability of the target, figure 5 suggests this may not be the case as the target molecule is eliminated following critical point drying to form an aerogel. Further work is thus needed to create aerogel substrates which are viable for calcein blue detection using SERS.

It is worth noting that the peak at 1030 cm^{-1} in figures 2-5 is likely due to methanol trapped in the gel pores as a result of the initial hydrolysis reaction. This is suggested by the decrease in peak intensity after washing the gels with UPDI water, as shown in figure 4. Further washing may result in even greater decrease in intensity of this peak and a greater overall signal to noise ratio.

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For further information

For further information, please email ***eatkins @Linfield .edu***

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