

Detection of calcein blue in silver modified silica sol-gels using SERS

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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.

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 three minutes and silver colloid (7.20 mL), prepared following modification of the Lee and Meisel citrate reduction method, was added. The mixture was stirred an additional 2 minutes, poured into plastic cuvettes, and allowed to age 24 hours. Aged gels were placed in vials containing calcein blue (5.6 mM) for at least 48 hours prior to SERS spectrum acquisition.

Instrumentation: SERS measurements were obtained using a custom Raman spectrometer having a 532 nm excitation beam and thermoelectrically cooled CCD.

Results

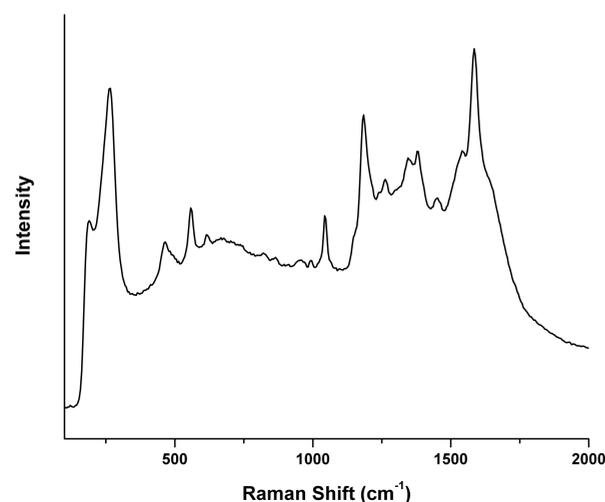


Figure 1: SERS spectrum of calcein blue solution (5.6 mM) combined with silver colloid in the presence of Na_2SO_4 aggregating agent

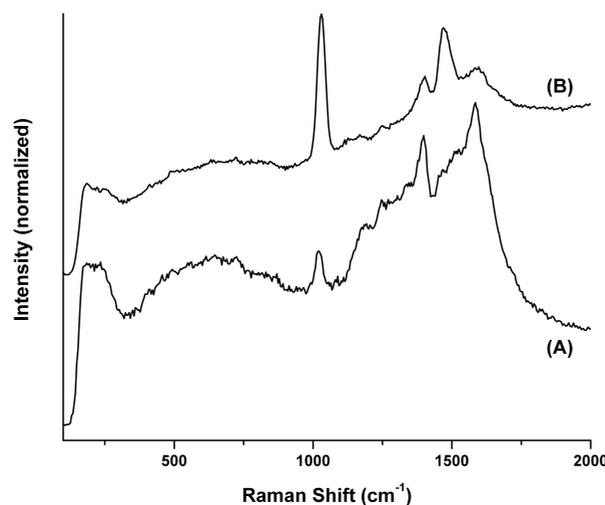


Figure 2: SERS spectra of a) a silica sol-gel containing silver colloid after 48 hour CB solution soak, and B) a silica sol-gel containing only silver colloid.

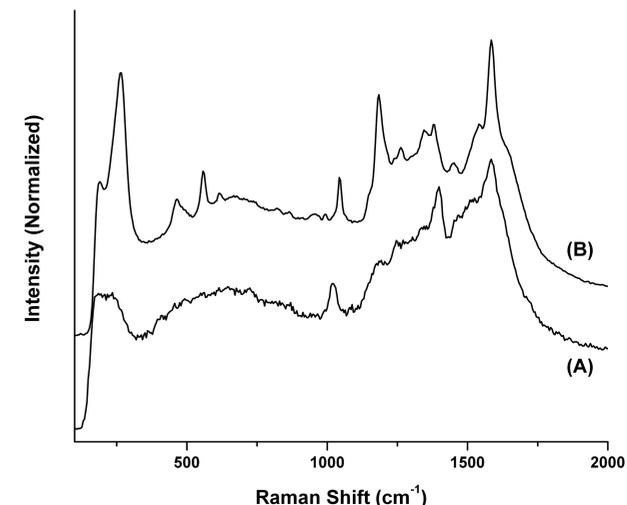


Figure 3: SERS spectra of a) a silica sol-gel containing silver colloid after 48 hour CB solution soak, and b) CB solution (5.6 mM) combined with silver colloid in the presence of Na_2SO_4 .

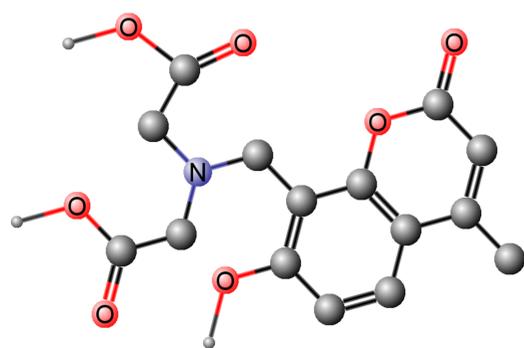


Figure 4: Molecular structure of calcein blue.

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. Alternatively, sol-gel sensing materials could be made by inclusion of calcein blue in the initial reaction mixture, which would confine the molecules in the gel matrix. Materials made in this manner would have different functionality and allow a wider range of applications for sensing materials comprised of modified sol-gels.

It is worth noting that the peak at 1030 cm^{-1} in figures 2a and 3a is likely due to methanol trapped in the gel pores as a result of the initial hydrolysis reaction. It may be possible to reduce the intensity of this peak by washing gels in water prior to addition of calcein blue to remove excess methanol from the gel pores. Alternatively, it may be possible to remove all unwanted liquids via supercritical drying of gel monoliths followed by rehydration in calcein blue solution.

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For further information

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