Optimization of 4-mercaptopentanoic acid in SiO₂-Ag colloid aerogels using surface-enhanced Raman spectroscopy

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Introduction
An aerogel is a porous, rigid solid composed of a light silica matrix. The term “aerogel” was coined by its creator Dr. Stephen Kratzer in the 1930s because the material is over 80% air, but has no gel-like properties in its aerogel form.

Silver nanoparticles were introduced into the silica matrix to make an enhanced surface that can be used with surface-enhanced Raman spectroscopy (SERS). A target molecule can adsorb to the silver particles within the silica matrix yielding a clearly enhanced Raman spectrum.

The target molecule, 4-Mercaptobenzoic acid (4-MCBA), was studied due to its two distinct functional groups that can adsorb to the silver either through the thiol or the carboxylic acid moiety. The target molecule was introduced into the silica matrix by direct mixing during sol gel formation and by adsorption into the acid- or base-catalyzed silver sol gels with different concentrations of 4-MCBA, prior to supercritically drying the sol gels.

Figure 1. 4-mercaptopentanoic acid

Materials and methods

Materials
Chemicals
The following chemicals were purchased from Sigma Aldrich (Milwaukee, WI), tetramethyl orthosilicate (TMOS, 98%), 4-Mercaptobenzoic acid (4-MCBA, 90%), silver nitrate (98%), and sodium citrate (95%). All reagents and solvents were analytical grade.

Silver colloid preparation
All glassware and containers were washed with aqua regia and deionized water before use. Silver colloids were made according to Lee and Meisel. Colloids appeared greenish brown with an extinction maximum of approximately 420 nm measured with UV-Vis spectrophotometry.

Sol Gel Synthesis
Sol gels were synthesized using adaptations to Rollison and Morris.

Surface Enhanced Raman Spectroscopy Measurements
SERS measurements were performed using a Raman microscope with a laser excitation at 532nm. SERS spectra were produced using 4-mercaptopentanoic acid mixed into the sol gels and resulting aerogels along with 4-mercaptopentanoic acid adsorbed onto the silver aerogels.

Figure 2. SERS spectrum of 4-MCBA on Ag colloid solution

Table 1. SERS peak assignments of 4-MCBA

<table>
<thead>
<tr>
<th>Raman Shift (cm⁻¹)</th>
<th>Peak Assignment</th>
<th>Notes</th>
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<tbody>
<tr>
<td>500</td>
<td>Mix of COO bending and C-COOH stretching</td>
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</tr>
<tr>
<td>508</td>
<td>Mix of COO bending and C-COOH stretching</td>
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<tr>
<td>1079</td>
<td>Ring breathing mode</td>
<td></td>
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<tr>
<td>1277</td>
<td>C-O stretch</td>
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<tr>
<td>1588</td>
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Conclusions
SiO₂-Ag colloid aerogels and sol gels appear to be viable SERS substrates for sensors. In this study it is seen that acid-catalyzed sol gels with 4-MCBA mixed into the silica matrix enhance the SERS signal more than the base-catalyzed sol gels. Figures 2 and 3 show very similar peaks that all come from 4-MCBA whereas Figure 4 shows peaks that come from ethanol and 4-MCBA. In a normal Raman spectrum of ethanol, the peaks at 1054 and 1079 cm⁻¹ are equal in intensity, but Figure 4 shows a more intense peak at 1079 cm⁻¹. This higher intensity is due to signal enhancement from ethanol and 4-MCBA. The enhancement factor of 4-MCBA adsorbed to the silver sol gels is between 10⁷ and 10⁸ when comparing the intensities of pure ethanol and 4-MCBA used. Other peaks such as 1154 cm⁻¹ and 1287 cm⁻¹ are also enhanced in Figure 4. From the absence of any peaks at 2931 cm⁻¹ in Figures 3 and 4 it can be concluded that 4-MCBA adsorbs through the sulfur of the thiol group.

The research conducted so far has touched on the two extremes for possible optimization techniques. Further research could involve finding other methods of adsorption, finding a more efficient way to deliver the 4-MCBA into the sol gel matrix, determining the time till complete saturation of the silver nanoparticles, and observing the effects of different pH environments.

Literature cited
[7] Figure 2 created by Katie Sours

Acknowledgments
We would like to thank the Linfield student-faculty collaborative research endowment and the M.J. Murdoch Charitable Trust. We thank Brian Gilbert and Elizabeth J.O. Atkinson for their help and support.

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Also reference the literature cited for further information on the experiments and research seen above.