Optimization of 4-mercaptobenzoic acid in SiO_2-Ag colloid aerogels using surface-enhanced Raman spectroscopy

Amy R. Cunningham, Dr. Elizabeth J.O. Atkinson, Dr. Brian D. Gilbert
Department of Chemistry, Linfield College, McMinnville, Oregon 97128

Introduction

An aerogel is a porous, rigid solid composed of a light silica matrix. The term "aerogel" was coined by its creator Dr. Stephen Kistler in the 1930s because the material is over 80% air, but has no gel-like properties in its aerogel form[4].

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 an 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.

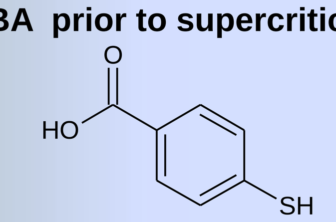

Figure 1. 4-mercaptobenzoic acid

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 (99.8%), and sodium citrate (90%). 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[5]. Colloids appeared greenish brown with an extinction maximum of approximately 420 nm measured with UV-VIS spectroscopy.

Sol Gel Synthesis

Sol gels were synthesized using adaptations to Rolison and Morris[6].

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-mercaptobenzoic acid mixed into the sol gels and resulting aerogels along with 4-mercaptobenzoic acid adsorbed onto the silver aerogels.

Results

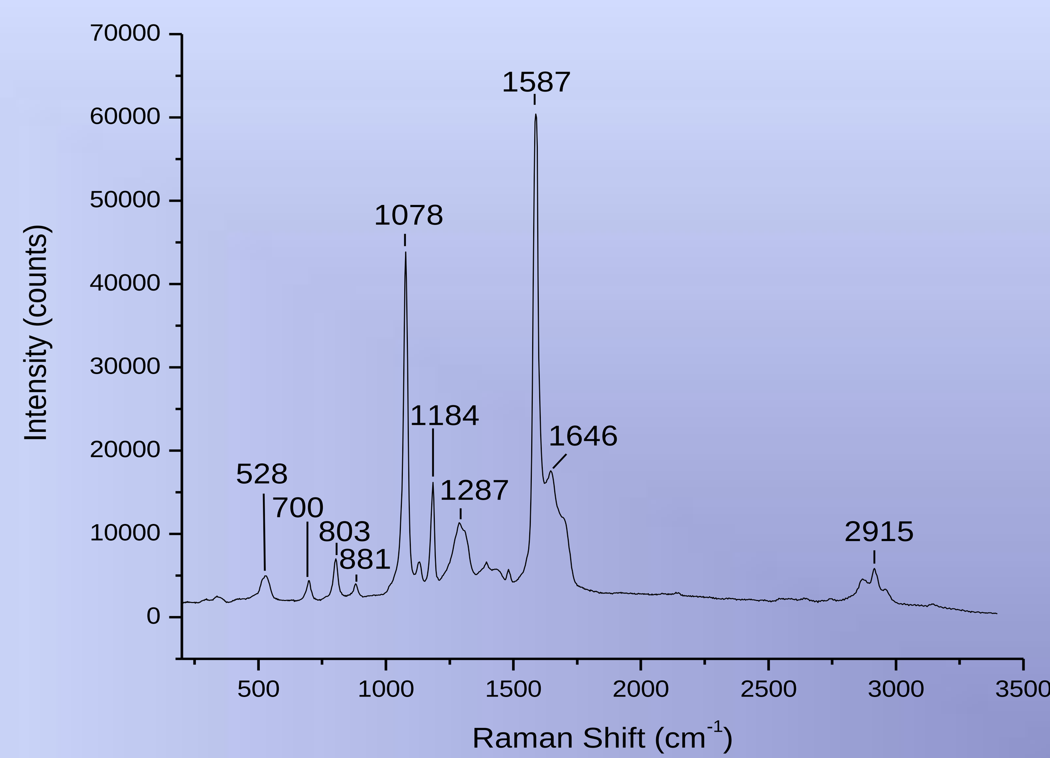

Figure 2. SERS spectrum of 4-MCBA on Ag colloid solution

Table 1. SERS peak assignments of 4-MCBA

Raman Shift (cm^{-1})	Peak Assignment[1,2,3,4]
800	Mix of COO- bending and C-COOH stretching
808	Mix of COO- bending and C-COOH stretching
1079	Ring breathing mode
1277	C–O stretch
1279	C–O stretch
1447	COO- stretch
1454	COO- stretch
1456	COO- stretch
1582	Ring breathing mode
1587	Ring breathing mode
1588	Ring breathing mode

Image 1. Custom –designed Raman microscope

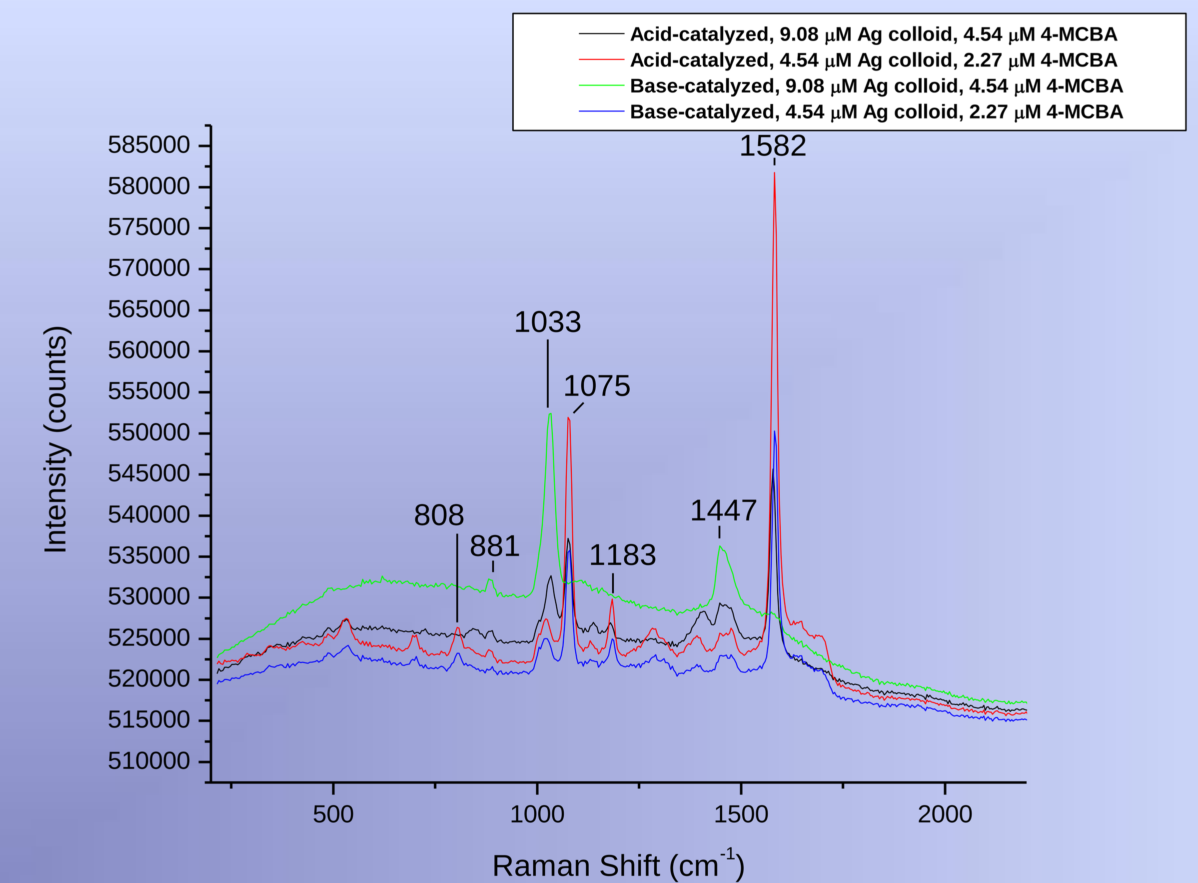

Figure 3. SERS spectra of acid- and base-catalyzed SiO_2-Ag colloid sol gels with 4-MCBA mixed within the matrix. Red and green lines show spectra of sol gels with 4.54 μM 4-MCBA and the black and blue lines show spectra of sol gels mixed with 2.27 μM 4-MCBA

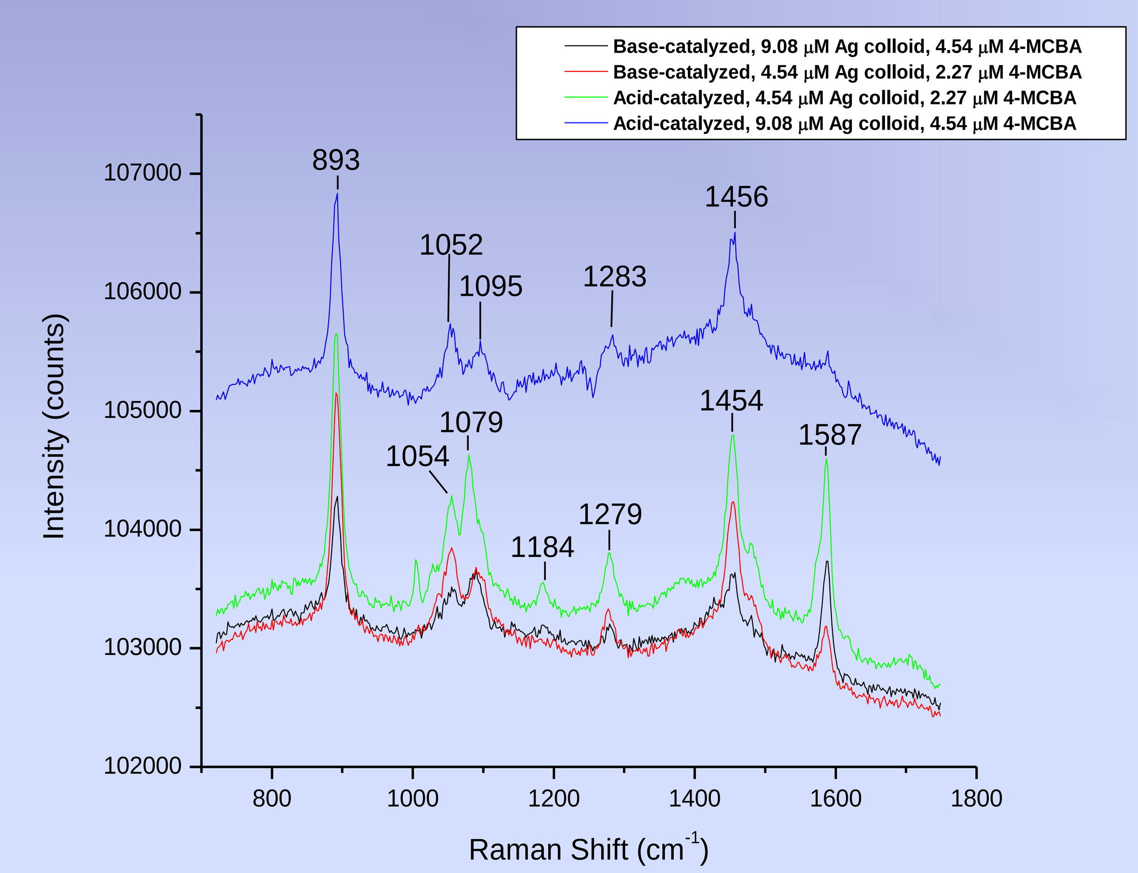

Figure 4. SERS spectra of acid- and base-catalyzed SiO_2-Ag colloid sol gels that have been submerged in 4-MCBA solutions for 10 days. The black and blue lines show spectra of sol gels that have been submerged in 4.54 μM 4-MCBA and the red and green lines show spectra of sol gels that have been submerged in 2.27 μM 4-MCBA

Conclusions

SiO_2-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 10^3 and 10^4 when comparing the molarities of pure ethanol and 4-MCBA used. Other peaks such as 1184 cm^{-1} and 1287 cm^{-1} are also enhanced in Figure 4. From the absence of any peaks at 2915 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.

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[7] Figure 2 created by Katie Sours

Acknowledgments

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For further information

Please contact *eatkins@linfield.edu* or *bgilber@linfield.edu*
Also reference the literature cited for further information on the experiments and research seen above.

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