

# Examination of acid- and base- catalyzed silica sol-gels, xerogels and aerogels containing silver nanoparticles and 4-mercaptobenzoic acid using surface-enhanced Raman spectroscopy

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## Introduction

Sol-gels are the precursors to both xerogels and aerogels, and have had increasing interest due to their potential applications. Research has been done on the gels and their potential use in controlled release drug delivery systems,<sup>1</sup> as potential gas sensors,<sup>2</sup> as well as in air purification, fire retardation, and sound insulation in buildings.<sup>3</sup>

Surface-enhanced Raman spectroscopy (SERS) is a well-established method for selective molecular identification and has been used in electrochemical, biological and chemical sensing.<sup>4</sup> It has even been looked at as a potential process for monitoring of chemical and/or biological weapons.<sup>5</sup>

4-Mercaptobenzoic acid (4-MBA, Figure 1) is a well-studied, pH sensitive, active SERS molecule. This makes it useful as a target molecule in the attempt to test base-catalyzed silica sol-gels as substrates for SERS and to determine how the 4-MBA reacts to different pH environments in the substrates.

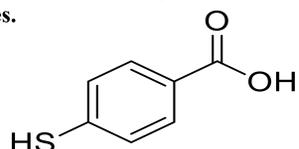


Figure 1: 4-mercaptobenzoic acid

## Methods

The following chemicals were purchased from Sigma Aldrich (Milwaukee, WI): tetramethyl orthosilicate (TMOS, 98%), 4-mercaptobenzoic acid (4-MBA, 99%), sodium citrate (90%), and silver nitrate (99.8%).

**Ag Colloid preparation:** All glassware was cleaned with Aqua Regia (3:1, conc. HCl:conc. HNO<sub>3</sub>), then rinsed with DI water. AgNO<sub>3</sub> (50 mL, 1mM) and DI water (25 mL) were brought to boil with stirring. Sodium citrate (7.0 mL, 1%) was added and the solution boiled (30 min). Upon completion, the solution was cooled to room temperature and stored in the refrigerator.

**Base-Catalyzed Sol-gel synthesis:** Methanol (5.52 mL), tetramethyl orthosilicate (1.92 mL), DI water (0.762 mL), and ammonium hydroxide (0.0052 mL, 30%) were combined and stirred for 10 min. Ag colloid (3.75 mL) was added, stirred for 10 min more before adding 4-mercaptobenzoic acid (3.75 mL). The solution was stirred for 5 min before pouring into plastic cuvettes to gel. Blank made by replacing 4-MBA with DI water.

**Acid-Catalyzed Sol-gel synthesis:** Tetramethyl orthosilicate (1.92 mL), methanol (1.13 mL), HCl (0.035 mL, 0.04 M), DI water (4.11 mL) and 4-MBA (3.75 mL, 2000 μM) combined and sonicated 10 min. Ag colloid and water were added with a combined volume of 3.75 mL, varying the amount of Ag, and solution sonicated 1 more minute.

**Aerogels and Xerogels:** Xerogels made by air-drying sol-gels. Aerogels made by supercritically drying sol-gels at 1350 psi and 38 °C.

**Surface Enhanced Raman Spectroscopy:** SERS spectra produced using a custom-built Raman spectrometer with a 532 nm laser. Spectra taken over 5 seconds with 50 nm slit size and an automatic background subtraction.

## Results

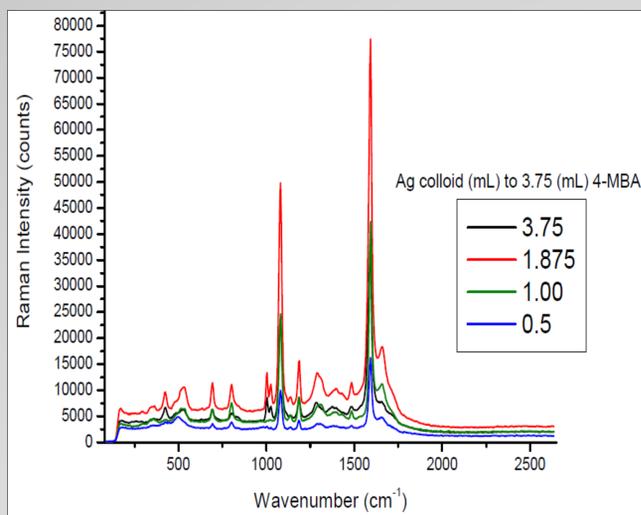


Figure 1: SERS of acid-catalyzed xerogels for select volumes of silver nanoparticles to a constant 4-MBA concentration (2000 μM)

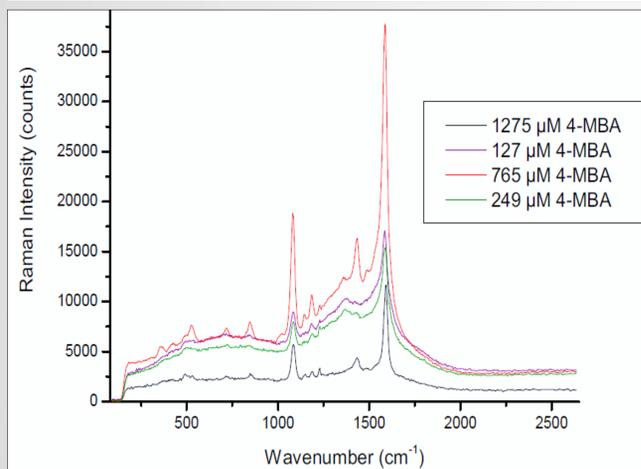


Figure 3: SERS of base-catalyzed aerogels for varying concentrations of 4-MBA to a constant concentration of silver nanoparticles (3.75 mL Ag colloid solution to 14.7072 mL sol-gel solution).

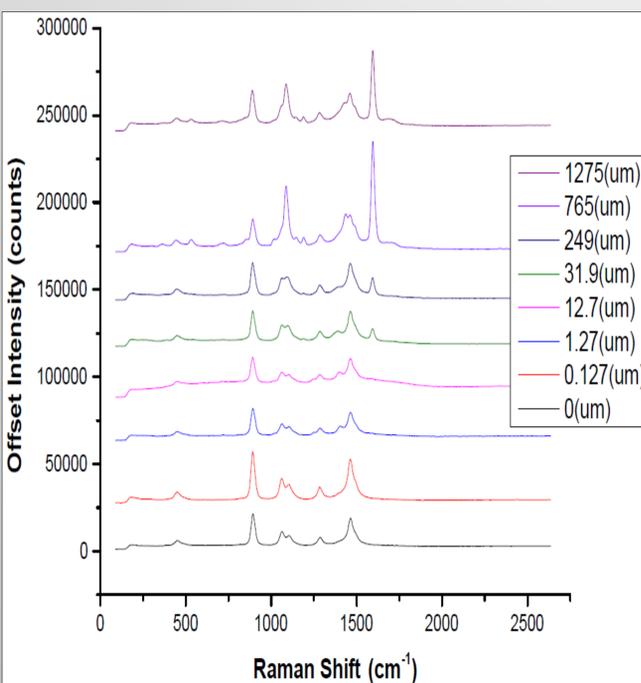


Figure 5: SERS of base-catalyzed sol-gels for varying concentrations of 4-MBA with a constant concentration of silver nanoparticles (3.75 mL Ag colloid solution to 14.7072 mL sol-gel solution).

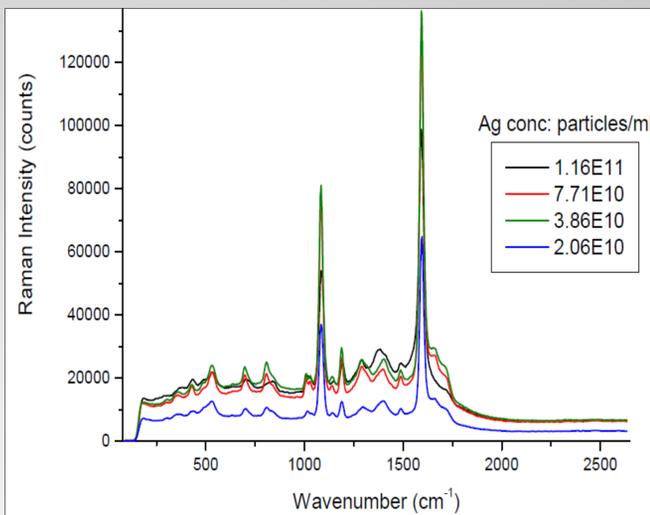


Figure 2: SERS of base-catalyzed xerogels for select volumes of silver nanoparticles to a constant 4-MBA concentration (2000 μM)

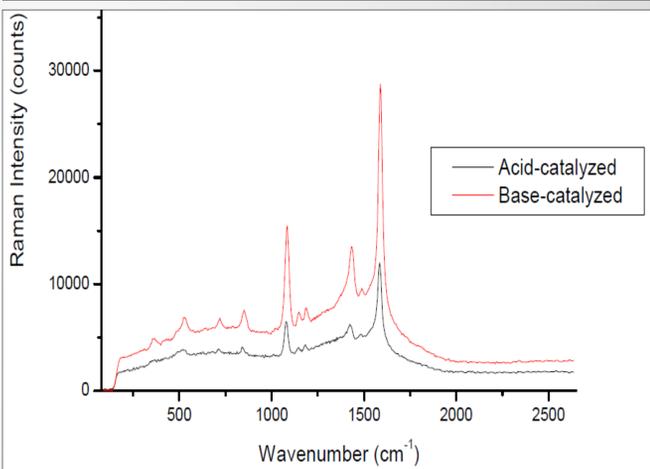


Figure 4: SERS of acid- and base-catalyzed aerogels for 1.875 mL of silver nanoparticles to a constant 4-MBA concentration (2000 μM)

Table 1: Peak Assignments for Surface Enhanced Raman Spectroscopy

SERS peak (cm <sup>-1</sup> )	Assignment <sup>5,6,7,8,9</sup>
718	Out-of-plane ring vibration
801	C-COOH stretch
879	C-C stretch
915	β(S-H)
1030	C-O stretch
1031	In-plane ring vibration
1079	CH <sub>3</sub> rocking
1080	In-plane ring vibration
1183	Aromatic COOH stretch
1370-1380	COO- stretch
1590	In-plane ring vibration
1623, 1710	C=O stretch
2580	S-H stretch

## Discussion

At all coverages of 4-MBA in the gels, there is no peak at 2580 cm<sup>-1</sup> (Fig. 1, 3, 5). This indicates the 4-MBA binds to the silver surface through the thiol group, which is consistent with earlier research.<sup>7</sup> From Table 1 and all 5 figures, we can see that in-plane ring vibrations are occurring. This indicates perpendicular orientation to the silver colloid. Tilting toward the silver surface may be caused by the interaction of COO-groups with the surface of the colloid. This is seen more at low concentrations and a more vertical orientation is expected to occur at higher concentrations.<sup>5</sup> These results also coincide with the environments effect on the 4-MBA. In Figures 1 and 2, the prominent differences in the state of the 4-MBA based on the different pH environments can be seen. The acid-catalyzed xerogels lack the size of the COO- peak at 1374 cm<sup>-1</sup> that is seen in the base-catalyzed spectrum.

This difference can't be seen in the aerogel comparison in Figure 4, which shows no significant peak differences between the two procedures. Figure 4 does indicate the base-catalyzed reaction may provide better spectra due to the larger intensity and sharper spectra.

As seen in Figure 5, the 4-MBA peaks start to become prominent at concentrations around 31.9 μM, with small signs at 1.7 and 12.7 μM.

In conclusion, the acid- and base-catalyzed silica sol-gels, xerogels, and aerogels seem to be successful SERS substrates. The 4-MBA seems to be more vertically oriented in the gels with slight tilting depending on the concentration, and the peaks also seem to adjust with the pH.

## Future Studies

Future investigations will look into potential acid-base sensor applications for the sol-gels, xerogels and aerogels.

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## Further Information

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