

# Surface-Enhanced Raman Scattering With Gold Core Silver Shell Nanoparticles

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# Introduction

Nanotechnology is becoming increasingly important and has many different applications; understanding the chemical and physical properties of matter in this size regime is therefore important. Gold and silver nanoparticles are particularly interesting because they are relatively simple to make and they provide a substrate for surface-enhanced Raman scattering (SERS). SERS can be used to characterize how molecules adsorbed to silver or gold nanoparticles are orientated and if they react on the surfaces.

# Introduction (cont.)

When making silver nanoparticles batch to batch variability of particle size and shape is high even though silver gives the best enhancement for SERS. This results in low reproducibility in SERS with silver. Gold nanoparticles are more consistent in shape from one batch to the next, but they do not give the enhancement that silver nanoparticles do. We are trying to address this limitation by making gold core silver shell nanoparticles that have the batch consistency of gold and enhancement close to silver. We are testing the SERS enhancement of the gold core silver shell nanoparticles with *p*-(dimethylamino) cinnamic acid (DMACA) and *p*-aminocinnamic acid (ACA).

# Experimental methods

## Gold and Silver Shell Gold Core (Ag@Au) nanoparticle preparation

All glassware was washed with aqua regia. Au particles were made first by adding 50 mL 38.8 mM trisodium citrate solution to 482.75 mL DI water and brought to a boil with vigorous stirring. Once boiling 17.25 mL 1% HAuCl<sub>4</sub> was added. The mixture was stirred and boiled for 15 min after a deep red color appeared, and then cooled to room temperature.

Ag@Au nanoparticles were made by adding 20 μmol of Au to a 50ml Erlenmeyer flask, boiling and adding the appropriate volume of 10mM AgNO<sub>3</sub> to produce desired mole fraction.

# Experimental methods (cont.)

## Surface Enhanced Raman Spectroscopy Measurements

0.05 mL colloid (Ag@Au, Ag or Au) and 0.05 mL  $\text{Na}_2\text{SO}_4$  (0.10 M) were combined with 0.05 mL of 1 mM DMACA or ACA to measure their SERS spectra utilizing a Raman spectrometer (laser excitation at 532 nm, 10 seconds exposure, 600 gr/mm grating and 30  $\mu\text{m}$  slits).

# Extinction Spectra

Fig. 1. shows the extinction spectra of both the  $\text{Ag}_5@Au_{95}$  and  $\text{Ag}_1@Au_{99}$ . They are characterized by the frequencies of their surface plasmon resonances, which occur at the peak wavelengths indicated in the Figure.

The single, narrow extinction band indicates formation of a monodisperse suspension of nanoparticles in solution. The plasmon resonance occurs at a wavelength similar to that of pure Au nanoparticles, but moves to the blue with increasing Ag.

# Extinction spectra

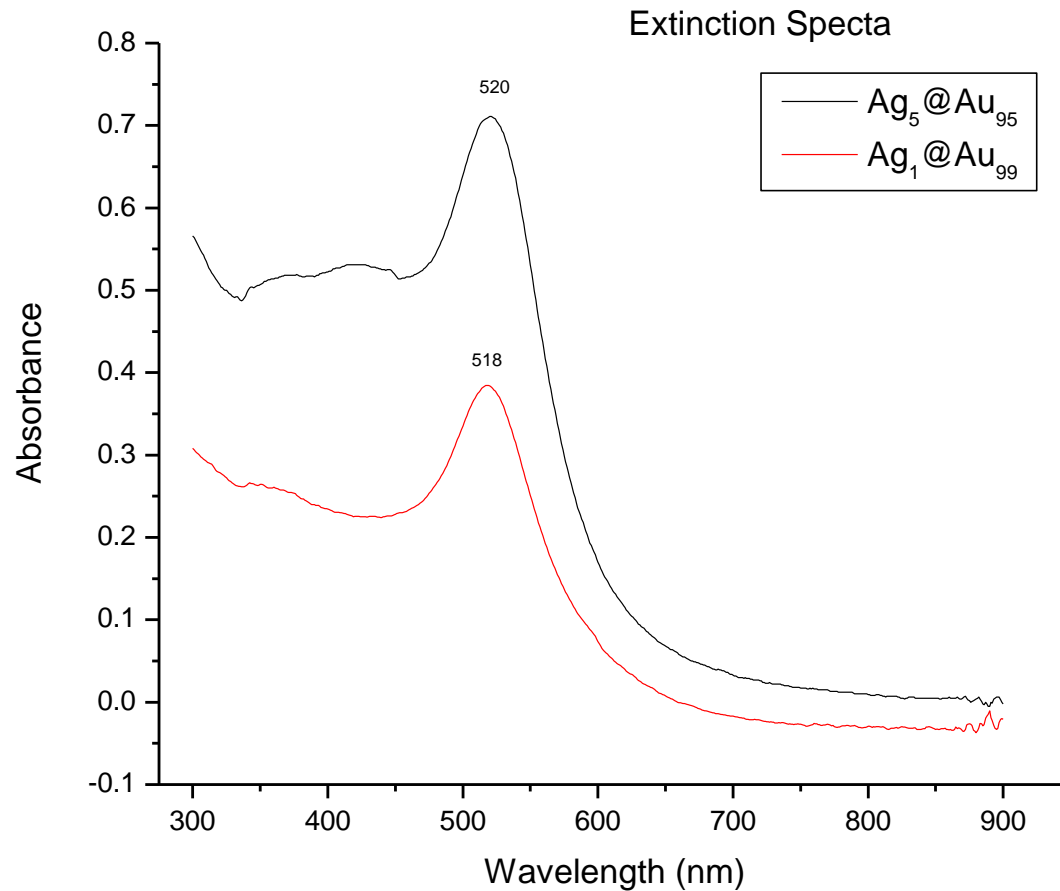


Figure 1. The  $\text{Ag}_1@Au_{99}$  nanoparticles have a peak at 518 nm, while the  $\text{Ag}_5@Au_{95}$  nanoparticles have a peak at 520 nm.

# DMACA SERS on Ag

The SERS spectrum of DMACA is shown in Fig. 2. The spectrum is dominated by bands at 1184, 1254 and 1594  $\text{cm}^{-1}$  and indicate that DMACA is oriented with respect to the Ag surface as shown in the figure. The COO<sup>-</sup> stretching band at 1370  $\text{cm}^{-1}$  indicates that DMACA's carboxyl group is deprotonated.

No bands due to the solvent (ethanol) are observed in the spectrum despite the fact that its concentration is much larger than that of DMACA.



# DMACA SERS

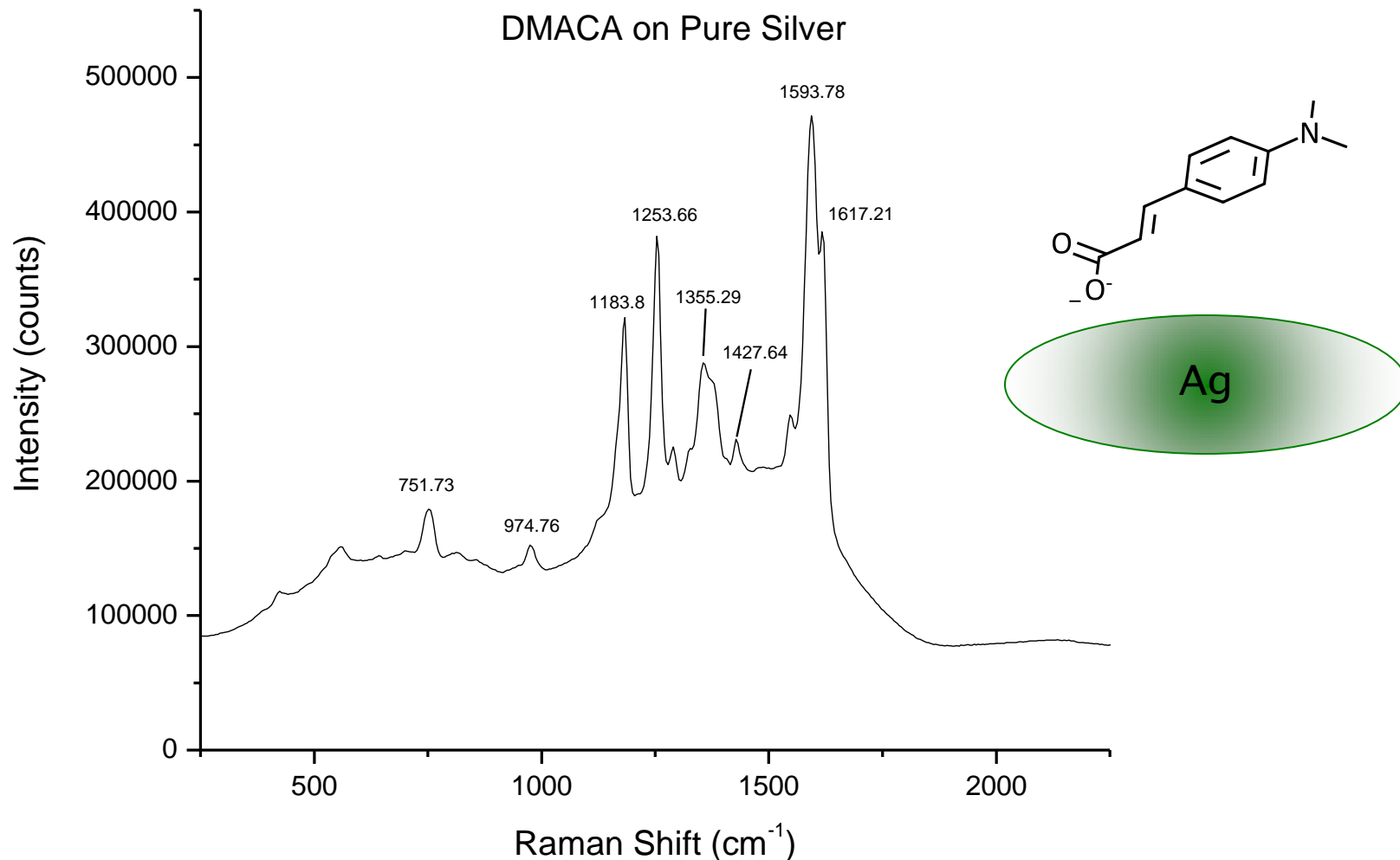


Figure 2. 1mM DMACA on pure Ag colloids.

# DMACA Ag@Au SERS

The SERS spectrum of DMACA on Ag<sub>5</sub>@Au<sub>95</sub> core shell nanoparticles is shown in Fig. 3. Bands due to DMACA are listed with their frequencies. The intensities of DMACA relative to the solvent (ethanol) peaks is much lower, indicating less enhancement of the signal on these nanoparticles than pure Ag. The spectrum does not contain enough information with which to determine the orientation of DMACA on the surfaces.

# DMACA core shell spectrum

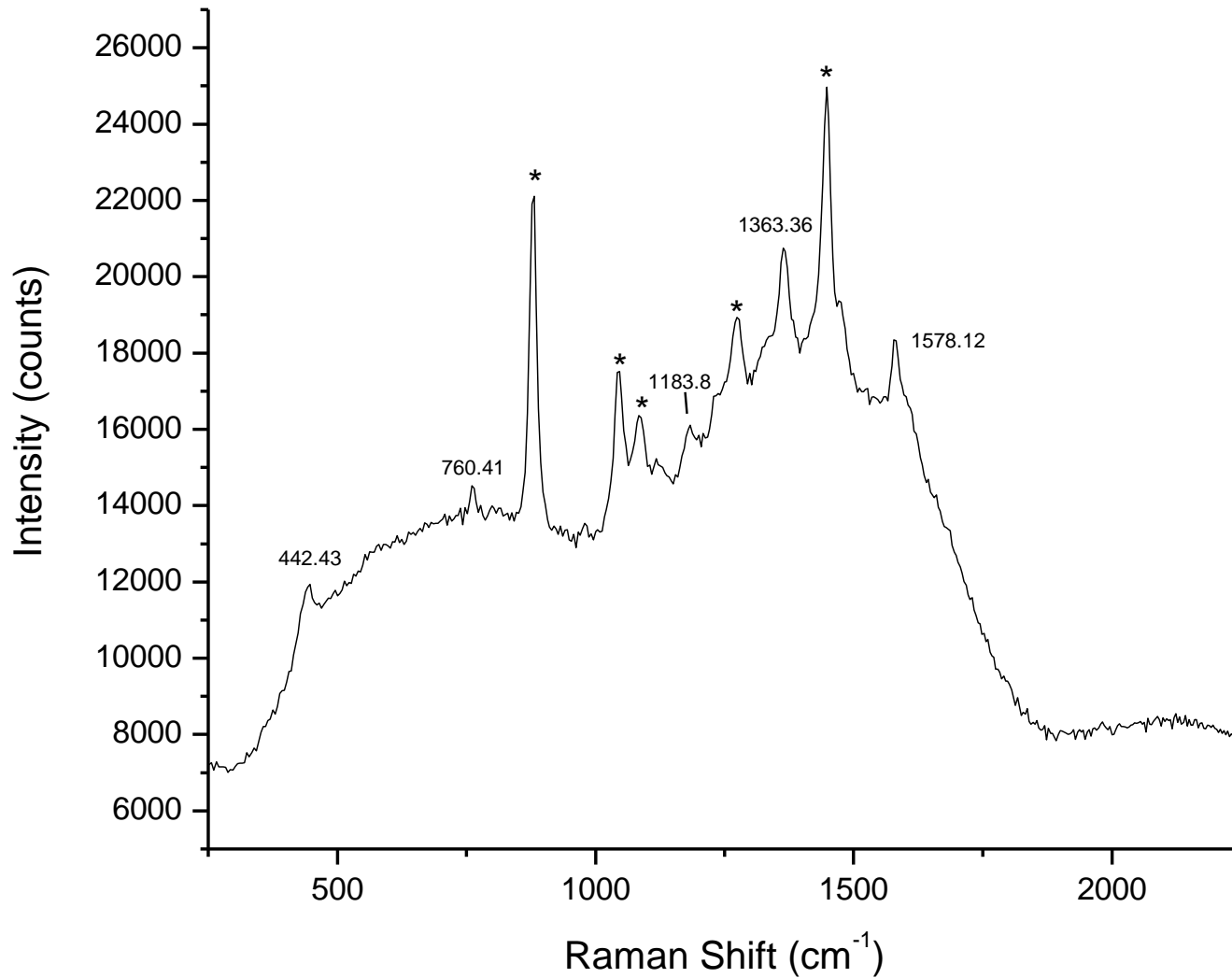


Fig. 3. 1 mM DMACA on Ag<sub>5</sub>@Au<sub>95</sub> colloids. \*indicate peaks due to ethanol.

# ACA SERS on Ag

The SERS spectrum of ACA is shown in Fig. 4. The spectrum is dominated by bands at 1175, 1245, 1371 and 1594  $\text{cm}^{-1}$ , which indicate that ACA is oriented with respect to the Ag surface as shown in the figure. The  $\text{COO}^-$  stretching band at 1371  $\text{cm}^{-1}$  indicates that ACA's carboxyl group is deprotonated.

No bands due to the solvent (ethanol) are observed in the spectrum despite the fact that its concentration is much larger than that of ACA.

# ACA SERS

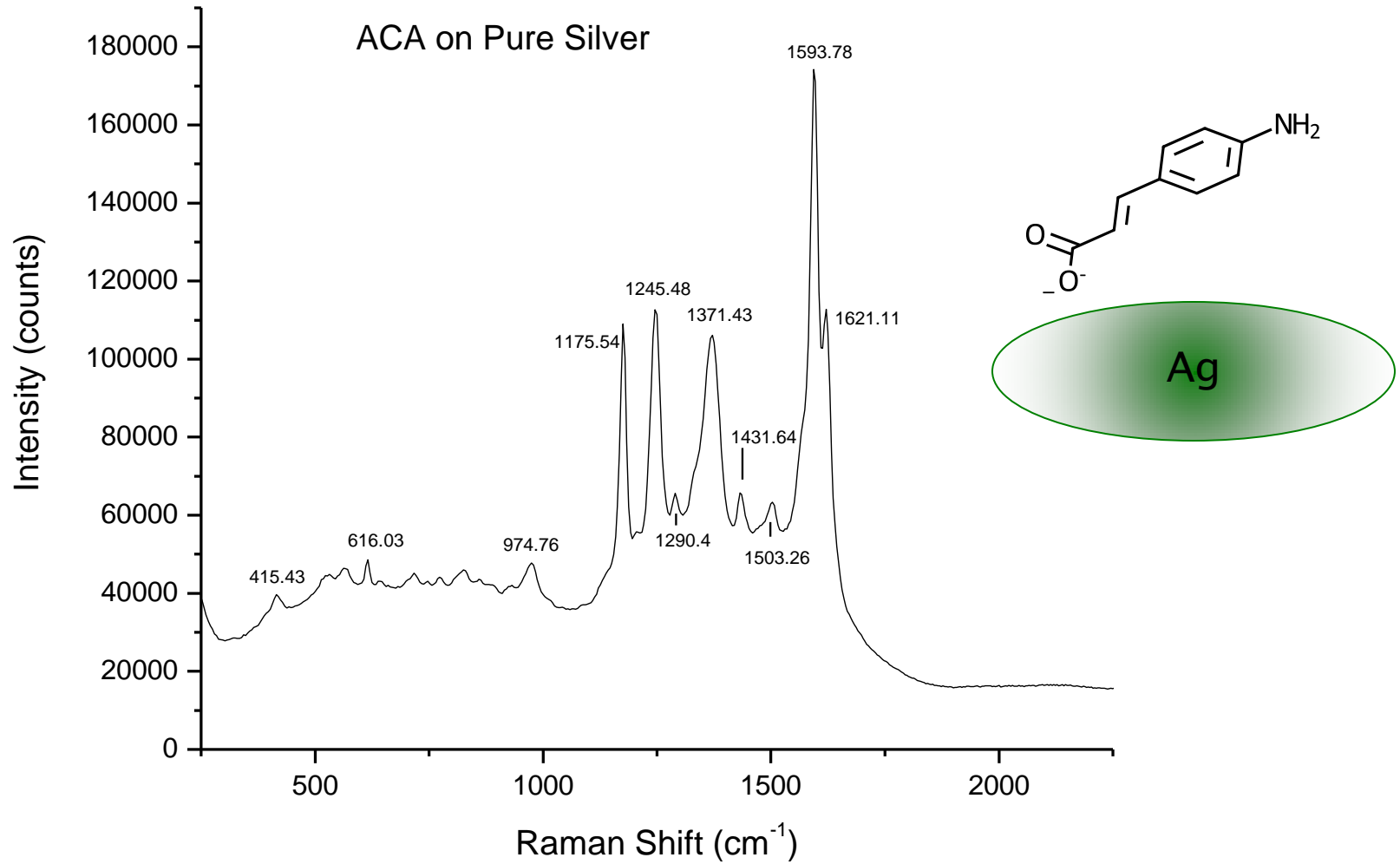


Figure 4. 1mM ACA on pure Ag colloids.

# ACA Ag<sub>1</sub>@Au SERS

The SERS spectrum of DMACA on Ag<sub>1</sub>@Au<sub>99</sub> core shell nanoparticles is shown in Fig. 5. Only one band due to ACA is observed, the band at 1594 cm<sup>-1</sup>. All of the other peaks observed are due to the ethanol (the solvent). Based on this, it appears that the Ag<sub>1</sub>@Au<sub>99</sub> nanoparticles provide little enhancement of the ACA SERS spectrum when compared with pure Ag.

# ACA core shell SERS

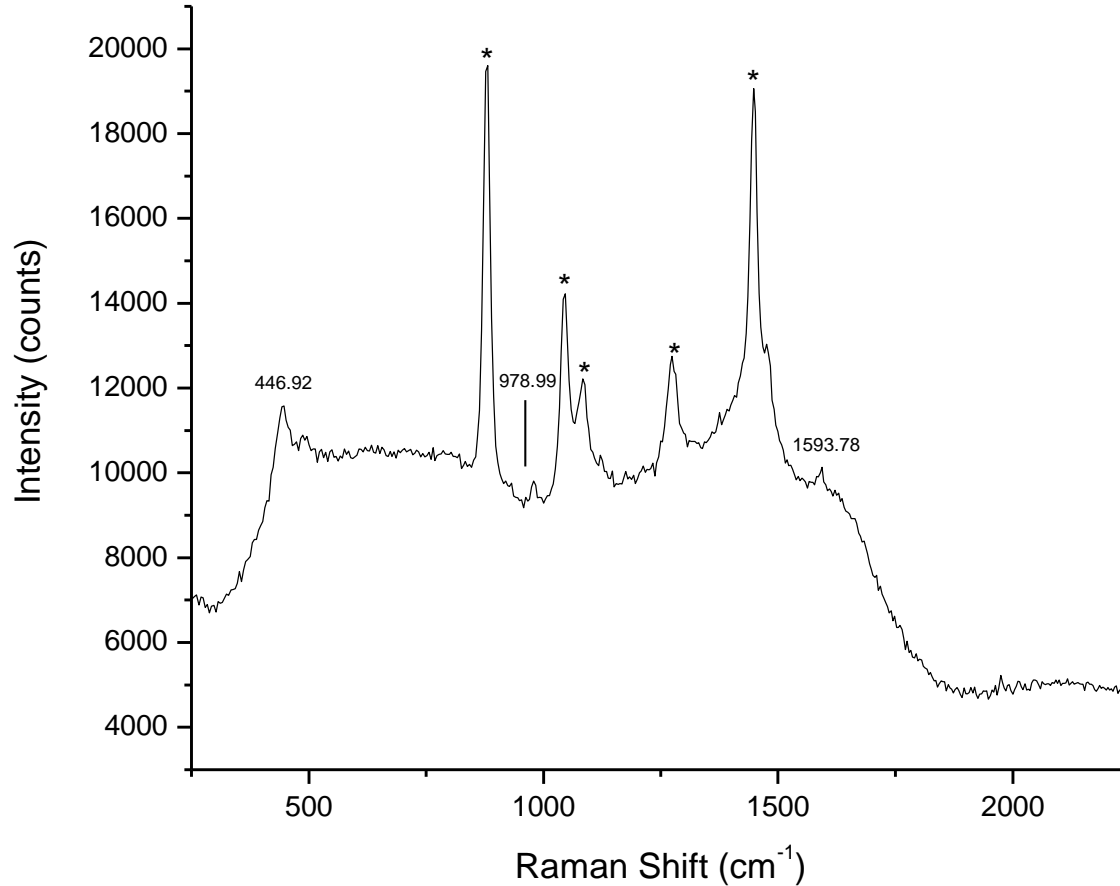


Figure 5. 1 mM ACA on Ag<sub>1</sub>@Au<sub>99</sub> colloids. \* indicate peaks due to ethanol.

# Conclusions

- ▶ Based on the extinction spectra we have produced Ag@Au nanoparticles with a relatively narrow size distribution. This may lead to more reproducible SERS spectra.
- ▶ SERS enhancement is much lower on the Ag@Au nanoparticles than for pure Ag. No SERS signal is observed with pure Au nanoparticles.
- ▶ SERS enhancement on Ag@Au nanoparticles appears to increase as the relative amount of Ag increases.



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