

Surface-Enhanced Raman Scattering of *p*-(dimethylamino)cinnamic acid on Silver and Silver-Gold Alloy Nanoparticles

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Introduction

We describe assignments for surface-enhanced Raman scattering (SERS) of 4-(dimethylamino)cinnamic acid (DMACA) on Ag and Ag₅₅-Au₄₅ alloy nanoparticles. DMACA is a push-pull charge transfer molecule that exhibits strong SERS signals at milli to micromolar concentrations. This makes DMACA a potentially useful molecule for SERS tagging in applications such as anti-counterfeiting and biomedical imaging.

SERS of were obtained on a range of silver-gold alloy nanoparticles with a range of chemical compositions. Evidence in the spectra indicates that the molecule adsorbs to the surface through the dimethyl amino group with the benzene ring tilted or standing up with respect to surface.

The SERS spectra of DMACA and 4-(dimethylamino)cinnamaldehyde (DMAC) on Ag nanoparticles are identical. We conclude that DMAC is oxidized on the surface to form DMACA on the basis of observed carboxyl vibrations in the surface.

Materials and Methods

Materials

DMACA (reagent grade) was purchased from Sigma-Aldrich. Solutions of DMACA were prepared in ethanol. Silver nitrate (99.9999%) was purchased from Sigma-Aldrich. Sodium citrate, sodium sulfate, magnesium sulfate, and sodium chloride (ACS reagent grade) were purchased from VWR. All materials were used as received.

Nanoparticle Preparation

Silver nanoparticles were prepared using the method described by Lee and Meisel [1]. Silver-gold alloy nanoparticles were prepared according to the method described by Link and El-Sayed [2]. Deionized water (18 MΩ) was used to prepare solutions. All glassware was cleaned with aqua regia and rinsed with deionized water prior to use. The resulting colloids were yellow-brown with an extinction maximum at approximately 420 nm, measured by UV-vis spectroscopy.

Raman and SERS measurements

Raman and SERS spectra were obtained using a home-built Raman microscope with laser excitation at 532 nm (150 mW), a 0.25 m monochromator and a thermoelectrically cooled (-20 C) CCD. SERS spectra were obtained by mixing DMACA with Ag and Ag₅₅-Au₄₅ colloids in glass microwell plates.

Results

Raman Spectra of DMACA with Ag and Ag₅₅-Au₄₅ colloids

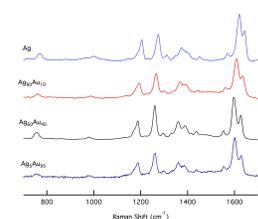


Figure 1. Raman spectra of DMACA with Ag and Ag₅₅-Au₄₅ colloids. Acquired with 1 sec. integration, 532 nm excitation, 20 mm slit.

The SERS spectra of DMACA are shown in Fig. 1, and vibrational band assignments are listed in Table I. The spectra are dominated by in-plane benzene ring vibrations, indicating that the benzene ring is standing up or tilted with respect to the nanoparticle surface. The observation of carboxyl group vibrations imply that the molecule adsorbs to the surface through the dimethyl amino group.

The SERS spectra indicate that nanoparticle compositions with higher percentages of silver provide the best enhancement for DMACA. It is interesting to note though that the best signal to noise ratio in the spectra is for the Ag₅₅-Au₄₀ alloy, and that even an alloy with only 5% Ag can significantly enhance the SERS of DMACA. This later observation is important, since alloys with higher fractions of Au are typically more stable, and easier to prepare.

Table I. Experimental and predicted vibrational frequencies of DMACA. (ν – stretch, δ – deformation)

Raman Shift (cm-1)	Vibrational Assignment
748	ν _{6a}
775	ν _{6a}
875	ν _{17b}
997	ν _{18a}
1140	ν _{16a} , ν _{16b}
1196	ν ₁₃
1267	ν ₃
1303	CH ₃ sym. rock
1338	ν ₁₄
1362	δ CH ₃
1382	ν(COO ⁻)
1438	ν _{16b}
1556	ν _{16a}
1604	ν _{9a}

Raman Spectra of DMACA and DMAC with Ag colloids

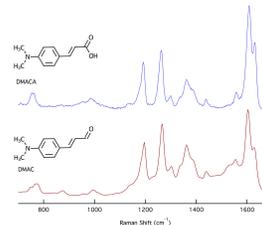


Figure 2. SERS spectra of DMACA (top trace, as in Fig. 1) and DMAC (bottom trace, 25 μM in 0.05 M Na₂SO₄, 10 sec. acquisition time, 50 μm slit) on Ag nanoparticles.

The SERS spectra of DMACA and DMAC on Ag nanoparticles are shown in Fig. 3. The DMAC spectrum was obtained after a solution of DMAC was mixed with Ag nanoparticles and sodium sulfate (to serve as an aggregating agent), and appeared immediately when acquired.

All of the vibrational peaks in the DMAC (bottom) trace can be assigned to DMACA vibrations. This observation, coupled with the absence of a C=O stretch which would appear at approximately 1630 cm⁻¹ leads us to conclude that DMAC is oxidized on the surface to form DMACA. This is consistent with the observation that (dimethylamino)benzaldehyde is oxidized to (dimethylamino)benzoic acid on silver and gold nanoparticles [3, 4].

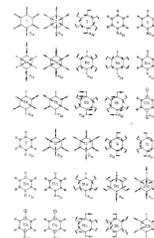


Figure 3. Normal vibrations of benzene from Varsanyi, "Vibrational Spectra of Benzene Derivatives", Academic Press, New York 1969.

Conclusions

We have made tentative vibrational assignments for DMACA SERS on Ag₅₅-Au₄₅ nanoparticles. Having the same concentration for each nanoparticle and keeping the acquisition time constant for each measurement, we observed spectra showing SERS response as a function of nanoparticle composition. SERS signals are strongest with greater Ag concentration in the alloys, however, Ag₅₅-Au₄₅ colloids show DMACA SERS intensity.

The absence of (dimethyl)amino vibrational modes, combined with the presence of carboxyl group vibrations and in-plane benzene ring modes in the SERS spectra indicate that DMACA adsorbs via (dimethyl)amino group with the benzene ring tilted or straight up with respect to the surface.

The SERS spectra of DMACA and DMAC on Ag nanoparticles are nearly identical. Therefore we conclude that DMAC is oxidized on the surface of the nanoparticles to form DMACA.

Literature Cited

- [1] Lee & Meisel, *J. Phys. Chem.* **86** 3391-3395 (1982)
- [2] Link & El-Sayed, *J. Phys. Chem. B* **103**, 3529 (1999)
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For Further Information

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