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

Ezgi Tannriver and Brian D. Gilbert

Department of Chemistry, Linfield College, McMinnville, Oregon 97128

Introduction

We describe assignments for surface-enhanced Raman scattering (SERS) of 4-(dimethylamino) cinnamic acid (DMACA) on Ag and \( \text{Ag}_{x}\text{Au}_{1-x} \) alloy nanoparticles. DMACA is a push-pull charge transfer molecule that exhibits strong SERS signals at milli- and micromolar concentrations. This makes DMACA a potentially useful molecule for SERS tagging in applications such as anti-counterfeiting and biomedical imaging.

SERS of DMACA 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 the surface.

The SERS spectra of DMACA and 4-(dimethylamino) cinnamic acid (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 spectra.

Materials and Methods

Materials

DMACA (reagent grade) was purchased from Sigma-Aldrich. Solutions of DMACA were prepared in ethanol. Silver nitrate (99.999%) was purchased from Sigma-Aldrich. Sodium citrate, sodium sulfate, magnesium sulfate, and sodium chloride (ACS reagent grade) were purchased from VWR. All materials were stable and easier to prepare.

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 Lin and El-Sayed [2]. Diamonized water (18 MD) 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 (350 mW), a 0.25 m monochromator, and a thermoelectrically cooled (-20 C) CCD. SERS spectra were obtained by mixing DMACA with Ag and \( \text{Ag}_{x}\text{Au}_{1-x} \) colloids in glass microvial plates.

Results

Raman Spectra of DMACA with Ag and \( \text{Ag}_{x}\text{Au}_{1-x} \) colloids

Figure 1. Raman spectra of DMACA with Ag and \( \text{Ag}_{x}\text{Au}_{1-x} \) colloids. Acquired with 1 sec. integration, 512 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 composition has a significant effect on the SERS signal. The SERS spectra of DMACA on Ag nanoparticles are nearly identical. Therefore we conclude that DMAC is oxidized on the surface of the nanoparticles to form DMACA.

Table I. Experimental and predicted vibrational frequencies of DMACA. (\( v \) = stretch, \( \delta \) = deformation)

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Experimental</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>794</td>
<td>795</td>
<td></td>
</tr>
<tr>
<td>1113</td>
<td>1116</td>
<td></td>
</tr>
<tr>
<td>1302</td>
<td>1302</td>
<td></td>
</tr>
<tr>
<td>1303</td>
<td>1303</td>
<td></td>
</tr>
<tr>
<td>1438</td>
<td>1438</td>
<td></td>
</tr>
<tr>
<td>1556</td>
<td>1556</td>
<td></td>
</tr>
<tr>
<td>1604</td>
<td>1604</td>
<td></td>
</tr>
</tbody>
</table>

Raman Spectra of DMAC and DMACA 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 Na\(_2\)SO\(_4\), 10 sec. acquisition time, 50 µm slit) on Ag nanoparticles.

The observation of carboxyl group vibrations imply that the benzene ring is standing up or straight up with respect to the surface.

Conclusions

We have made tentative vibrational assignments for DMACA SERS on \( \text{Ag}_{x}\text{Au}_{1-x} \) 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, \( \text{Ag}_{x}\text{Au}_{1-x} \) 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)amine 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


Acknowledgments

• Linfield College student-faculty collaborative research endowment for funding.
• Blatic Chemist for the preparation of \( \text{Ag}_{x}\text{Au}_{1-x} \) nanoparticles

For Further Information

Please contact bgilber@linfield.edu.