

## Development of silver film *via* thermal decomposition of layered silver alkanecarboxylates for surface-enhanced Raman spectroscopy

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**This work demonstrates that optically tunable, SERS-active Ag films can be reproducibly fabricated on glass by the thermal decomposition of layered silver alkanecarboxylates.**

Noble metallic nanostructures exhibit a phenomenon known as surface-enhanced Raman scattering (SERS) in which the scattering cross sections are dramatically enhanced for molecules adsorbed thereon.<sup>1</sup> Thanks to the enormously large enhancement factor (EF) on the order of  $10^6$ , one can readily acquire the vibrational spectra from adsorbates on roughened surfaces of Ag, Au and Cu.<sup>2</sup> In recent years, it has been reported that even single molecule spectroscopy is possible by SERS, suggesting that the EF can reach as much as  $10^{14}$ – $10^{15}$ .<sup>3</sup>

To use SERS in routine, on-line studies for analytical purposes,<sup>4</sup> the substrates should be stable, reproducibly prepared, inexpensive, and easy to make. In reality, the enhancement properties of a SERS-active surface are highly susceptible to its method of preparation and therefore its detailed nanostructure. Most SERS-active surfaces currently available are thus lacking in stability and/or reproducibility. Electrochemically roughened electrodes<sup>5a</sup> usually exhibit poor reproducibility. SERS substrates obtained by chemical methods<sup>5b</sup> are not clean due to organic contaminants. Vacuum-evaporated metal island films<sup>5c</sup> should be prepared with the evaporation rate and mass thickness of the corresponding metals controlled to obtain the best SERS enhancement; the system is also expensive.

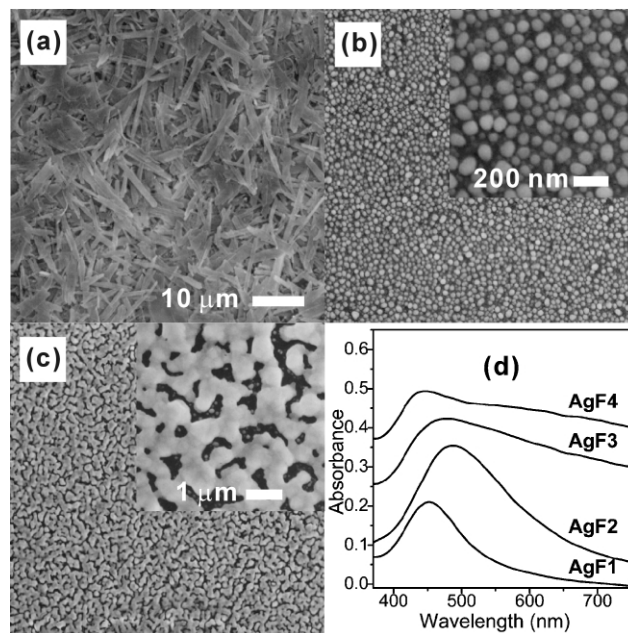
We have reported previously that alkanic acid-derivatized Ag nanoparticles are produced upon heat treatment of layered silver alkanecarboxylates,<sup>6a,b</sup> and found separately that the organic moieties anchored on the Ag nanoparticles are completely removed by heating to 750 K.<sup>6a,c</sup> On these grounds, we report in this communication that optically tunable, SERS-active Ag films can be reproducibly fabricated on glass microscope slides by the thermal treatment of silver stearate ( $\text{AgOOC}(\text{CH}_2)_{16}\text{CH}_3$ , AgSTA) at 750 K. The nanostructured Ag films prepared in this way are expected to provide a new type of substrate material for developing SERS as an ultra-sensitive analytical tool.

Fig. 1(a) shows a typical scanning electron microscope (SEM) image of the AgSTA film† before the thermal treatment; SEM images of the Ag films were measured using a JSM 840-A scanning electron microscope at 20 kV. Micrometer-sized platelets were characterized previously to reflect a layered structure with an interlayer spacing of  $\sim 50$  Å.<sup>6a</sup> Upon heating to 500 K ( $10 \text{ K min}^{-1}$ ) under an  $\text{N}_2$  atmosphere ( $110 \text{ ml min}^{-1}$ ), STA-capped Ag nanoparticles with uniform size distribution ( $\sim 4$  nm) are produced from the salt; the glass slide thus becomes dark-brown. If a film quenched from 500 K is immersed in toluene, STA-capped Ag nanoparticles are dissolved into the solvent. The solution then exhibits the characteristic surface plasmon absorption of Ag particles at *ca.* 417 nm.<sup>7</sup>

As the AgSTA film is continuously heated up to 750 K, the STA-capped Ag nanoparticles gradually lose organic moieties due to thermal decomposition. At the same time, due to the enhanced mobility, the particles collide with one another to produce larger particles or islands. When the film was cooled

back to room temperature, it was colored a yellowish-white. Once the film is rinsed with ethanol, hardly any organic contaminant was detected in the IR and Raman spectra (data not shown), suggesting that the film is free from thermal decomposition products.† The SEM image of the AgF1 film is shown in Fig. 1(b). The film consists of spheroidal particles with an average particle size of  $100 \pm 20$  nm; nonetheless, relatively small particles ( $< 50$  nm) are also present as can be seen from the inset. The morphology of the AgF2 and AgF3 films was very similar to that of AgF1 except that the average particle size was estimated to be  $150 \pm 20$  nm. The surface morphology of the AgF4 film is, however, totally different from that of AgF1. This can be evidenced from the SEM image shown in Fig. 1(c) which consists of wire-like networks instead of spheroids. These observations suggest that the surface morphology of the nanostructured Ag film is dependent on the amount of AgSTA spread initially on the glass slide.

Fig. 1(d) shows normal incidence, unpolarized UV/Vis spectra (SINCO S-2130 spectrophotometer) of the AgF1, AgF2, AgF3 and AgF4 films. For the AgF1 film, a narrow absorption maximum is seen at *ca.* 458 nm, which can be attributed to the surface plasmon resonance of uniformly distributed nanosized-Ag particles.<sup>8</sup> In the case of AgF2, the absorption maximum is red-shifted to 480 nm. Presumably, this is associated with the increase in the particle size from 100 to 150 nm. More dramatic changes are observed for AgF3 and AgF4. The absorption maxima are blue-shifted from 480 to 460 and 440 nm, respectively, for AgF3 and AgF4. Furthermore, significant band broadening occurs for both films toward the red. It has been well



**Fig. 1** SEM images of (a) AgSTA and its thermal reaction products (b) AgF1 and (c) AgF4 films on glass; the insets in (b) and (c) show the magnified images. (d) Normal incidence, unpolarized UV/Vis spectra of the nanostructured Ag films. See text.

documented in the literature that densely packed particle arrays, either periodic or random, exhibit surface plasmon resonance features that are broadened considerably by dipole–dipole interactions and can have either red- or blue-shifted excitation spectra compared with those of isolated particles.<sup>9</sup> The optical absorption patterns for our four films are quite similar to those of the annealed Ag island films;<sup>9b</sup> the absorption intensities are overall ~50% lower in our films, however. These observations would indicate that the nanostructured Ag films could be tuned to possess specific surface plasmon band(s) ranging from the green to the red region. Referring to the electromagnetic mechanism of SERS,<sup>10</sup> this implies that a wavelength-dependent SERS-active substrate can be fabricated simply by varying the amount of AgSTA spread initially on the glass slide before heat treatment.

We evaluated the performance of our silver structures as SERS substrates using benzenethiol (BT) as a model compound.† The AgF1 film exhibited strong enhancement efficiency at 514.5-nm excitation. No signal, even very weak, could be detected using the 632.8-nm radiation, however. In contrast, the AgF4 film showed strong enhancement at 632.8-nm excitation while a negligible signal was detected at 514.5-nm excitation. For the AgF2 and AgF3 films, moderate SERS spectra could be obtained at both 514.5- and 632.8-nm excitation wavelengths; more enhanced signals are actually observed using the 514.5- and 632.8-nm radiation, respectively, for AgF2 and AgF3, as can be seen in Fig. 2; this clearly reflects the different optical absorption characteristics of the two films. The size-dependent enhancement behavior for Ag particles reported by Maxwell *et al.*<sup>11</sup> are in conformity with our observation that the AgF1 and AgF3 films are, for instance, highly suitable for visible SERS.

The SERS spectrum on our films was highly reproducible; the relative standard deviation was determined to be 8.9% for AgF1, 14.1% for AgF2, 21.6% for AgF3, and 9.8% for AgF4 from three different measurements for each type of films with three different spots per film. The quality of the films was hardly affected by immersing in water or ethanol for up to 24 h. The films also withstand prolonged sonication in water and ethanol. Although the films can be peeled off with tape, the extent of detachment is far smaller compared with the case of a vacuum-evaporated island film. Regarding the SERS EF, we obtained an enhancement of  $1.2\text{--}5.8 \times 10^5$  for the AgF1 film, based on the  $1573\text{ cm}^{-1}$  peak of BT; this was reproducibly observed in six different measurements. The stability as well as the reproducibility of our films may be associated with the earlier report by Van Duyne *et al.*<sup>9b</sup> that the SERS activity of Ag island films is not lost when they are subjected to quite vigorous thermal annealing conditions (*viz.*, 600 K for 60 min).

In summary, we have discovered that very stable and optically tunable, SERS-active Ag films can be fabricated

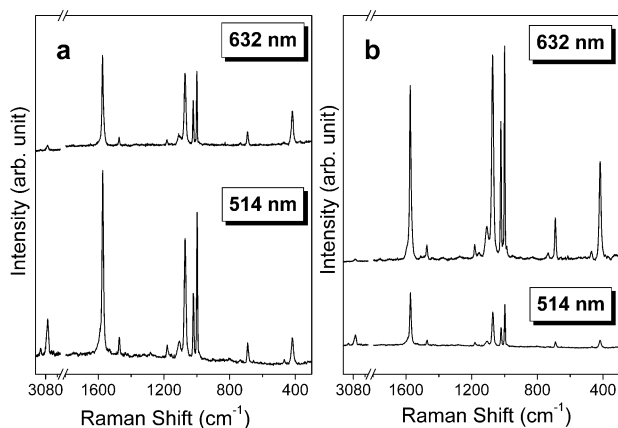
reproducibly simply by the thermal decomposition of layered AgSTA on glass. Further studies are underway to determine the optimum conditions to prepare more precisely tuned SERS-active substrates. We believe that such substrates must be useful particularly in high temperature applications such as *in situ* heterogeneous catalytic studies and combined thermal desorption/SERS investigations in UHV experiments.

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## Notes and references

† AgSTA was prepared in powdered form by the two-phase method; details were reported previously.<sup>6a</sup> AgSTA (25 mg) was subsequently dispersed in toluene (10 mL), and subjected to sonication for 20 min. An aliquot of the resulting AgSTA suspension was then spread evenly on the pre-cleaned glass slides ( $10 \times 10$  mm). The platelets of AgSTA consist of alternate regions of hydrophilic Ag–COO groups and hydrophobic alkyl chains. At the initial stage of solvent evaporation, the platelets near the glass substrate are presumed to adhere to the substrate *via* the hydrophilic part of the platelets. Subsequent deposition will proceed mainly through the hydrophobic interaction between different platelets, resulting in a quite uniform AgSTA layer on a glass slide. On these grounds, specifically, 20, 40, 60 and 80  $\mu\text{L}$  were spread on four different glass slides in this experiment corresponding to 0.05, 0.11, 0.14 and 0.19 mg of AgSTA, respectively. These films correspond to vacuum-deposited Ag island films formed on glass substrates with mass thicknesses of 7, 15, 19 and 26 nm, respectively (the four Ag films derived from 0.05, 0.11, 0.14 and 0.19 mg of AgSTA are denoted AgF1, AgF2, AgF3 and AgF4, respectively).

‡ Raman spectra were acquired using a Renishaw Raman system 2000 spectrometer equipped with an integral microscope (Olympus BH2-UMA). Either the 514.5-nm radiation from an air-cooled Ar<sup>+</sup> laser (Spectra Physics model 163-C4210) or the 632.8-nm radiation from an air-cooled He/Ne laser (Spectra Physics model 127) was used as the excitation source. The typical laser power at the sampling position was 0.2 mW for the 514.5-nm line and 0.17 mW for the 632.8-nm line with an average spot size of 1  $\mu\text{m}$  in diameter. To record the SERS spectrum of benzenethiol (BT), an aliquot of 10  $\mu\text{L}$  BT ( $2 \times 10^{-4}$  M) in methanol was spread on the Ag film. After evaporation of the solvent the SERS spectrum was recorded under ambient conditions. The data acquisition time was usually 30 s.



**Fig. 2** SERS spectra of benzenethiol adsorbed on (a) the AgF2 and (b) AgF3 films on glass.

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