Surface-Enhanced Raman Scattering Spectroscopy of Single Carbon Domains on Individual Ag Nanoparticles on a 25 ms Time Scale

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Surface-enhanced Raman scattering (SERS) spectroscopy on single nanoparticles[1,2] and even single dye molecules on isolated nanoparticles[3,4] has drawn significant recent interest. Using single dye molecules, Kneipp[3] and Nie[4] have shown that SERS can increase the scattering cross-section to the point where it renders the strength of the spectroscopic signal comparable to that of single molecule fluorescence.[5] The ability to detect the Raman signal from single molecules can only be possible by a dramatic amplification of the Raman scattering cross-section.[6]

In this paper we report on confocal microspectroscopy of first- and second-order Raman scattering from carbon nanocrystallites adsorbed on single, isolated Ag nanoparticles. We show that the Raman signal of a very low number of carbon crystallites (probably one) with a two-dimensional domain size of typically lower than 10 nm can be recorded. Additionally, we spectrally capture—on a 25 ms time scale—the previously reported SERS blinking effect[4] and show that the blinking is most likely due to a thermally induced diffusion of the carbon nanoparticles through a SERS active "hot spot" on the Ag nanoparticle. Finally, in direct contrast to the low SERS-active efficiency reported by Nie and Emory,[4] we observe that more than 75% of our Ag nanoparticles are SERS active. We propose that the morphological difference in Ag nanoparticles between our study and theirs is most likely responsible for this difference.

The substrates used are glass microscope slides coated with approximately 180 nm of indium−tin-oxide (ITO). Samples are electrochemically prepared on the ITO from a silver nitrate/potassium cyanide solution using a potentiostatic double pulse method.[7] Figure 1 shows a scanning electron micrograph (SEM) image of the particles on the ITO surface. The cauliflower-like shape shows that their morphology is not homogeneous and that they are clusters of Ag crystallites. This cauliflower shape may explain the fact that more of our Ag nanoparticles are SERS active than the faceted Ag nanoparticles used in other studies.[4]

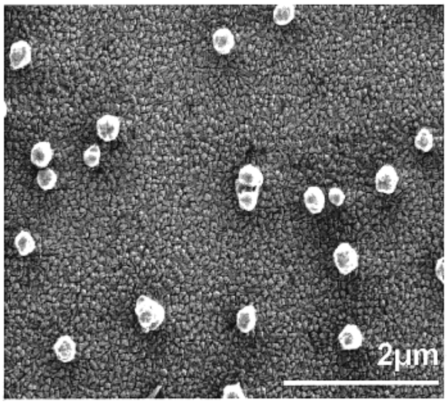

Figure 1. Scanning electron microscopy image of electrochemically grown Ag nanoparticles on ITO-on-glass substrate.

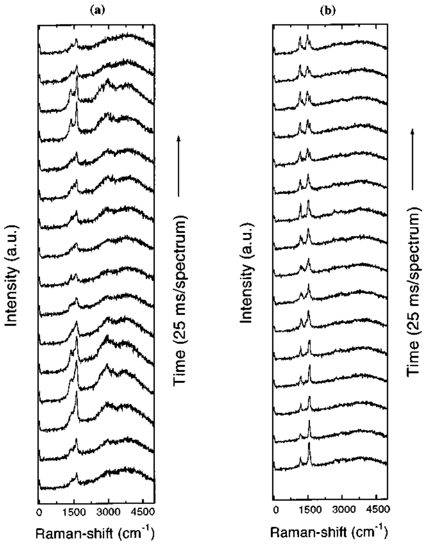

Figure 2. Temporal progressions of spectra acquired under 532 nm illumination for carbon domains on two separate isolated Ag nanoparticles. Each spectrum was acquired using a 25 ms integration time such that the collection time for each progression was very nearly 400 ms. The bottom spectra were acquired during the first 25 ms, and the top spectra were acquired during the last 25 ms. Differences between series a and series b are discussed in the text.

The Raman spectra are acquired with 532 nm excitation. Epi-fluorescence (backscattered micro-Raman) geometry is used. The objective (40×, 0.65 NA) provides a diffraction-limited spot size approximately 1 μm in diameter, and the maximum power density on the sample is roughly 10^6 W/cm^2. The spectral resolution of the experiment is approximately 30 cm^{-1}.

Figure 2 depicts two progressions of Raman spectra; each series is from a single isolated nanoparticle, with each individual spectrum acquired with an integration time of 25 ms. The bottom spectra are integrated over the first 25 ms, the second spectrum from the bottom is the next 25 ms, and so on. Spectra were also acquired with 488 nm excitation to prove that the sharp peaks at 1590 and 1380 cm^{-1} and the broad peak in the 2500−3000 cm^{-1} range are Raman in nature. The broader band above 3000 cm^{-1} is fluorescence from the ITO substrate.

The Raman peaks are a result of agglomeration of carbon atoms forming nanocrystalline carbon domains on the Ag particle surface. The peaks are in excellent agreement with those of finite graphite crystal size.[8−12] Extensive SERS studies were carried out with carbon layers on silver[13] and with variously treated

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graphite samples with deposited silver films coated on top. In these previous studies, the aims were (1) to develop a highly sensitive surface probe[14,15] and (2) to explore the mechanisms of SERS.[16,17] Our spectra are interpreted as follows: The higher-energy mode (1590 cm^{-1}) is the typical Raman-active band of highly ordered macroscopic graphite crystals which is associated with in-plane atomic displacement and has E_{2g}-symmetry. The line at ~1380 cm^{-1} is the symmetry forbidden *D*-band which becomes active with the relaxation of the wave vector conservation in nanocrystalline and glassy carbon.[8,9] Tuinstra and Koenig have found a relation between the intensity ratio of these bands and the in-plane domain size of carbon crystallites.[8] With decreasing domain size, the 1380 cm^{-1} line grows with respect to the 1590 cm^{-1} line, and both lines shift to higher energies, and their widths increase.[18] From our spectra we hence conclude that the 2D domain size must be on the order of 10 nm or smaller. The source of the carbon can easily be traced to the sample fabrication solutions by higher quality rinsing, which results in disappearance of the Raman bands. Our energy-dispersive X-ray (EDX) spectra indicate roughly 10% of the surface atoms are carbon.

Series a from Figure 2 is representative of most of the hundreds of Ag nanoparticles that we have studied. Series b represents less than 10% of the particles we have studied. The most significant differences in the two spectral progressions include: (1) the fluctuating time dependence of series a versus the more stable series of b, (2) the absence of a second-order peak in series b, and (3) the narrower line widths of the spectra in series b.

The spectral blinking is believed to be a result of a thermally activated diffusion of the carbon domain through a local hot spot on the Ag nanoparticle. That is, not every region of the Ag particle is SERS active, but rather, just one (or a small number of regions) is hot, where the enhancement increases significantly. The fact that the series of Figure 2a is time dependent indicates that no more than a few carbon domains are present. More than a few carbon domains would yield spectra that ensemble averaged such that the variations would not be observed. Further, we speculate from the stability and the time dependence of the Raman bands in Figure 2b that a carbon sheet is formed on the Ag nanoparticle. These Raman spectra are consistent with the sheet remaining on the hot spot while varying in thickness—probably via a folding of the sheet or other rearrangement of the carbon atoms comprising the sheet. The spectral modes and peak splitting are consistent with this premise.

Consider the broad spectral features in the 2500−3000 cm^{-1} range of Figure 2a. This is the typical second order Raman regime of graphite and nanocrystalline carbon where we expect overtones and combinations of the previously observed lines. According to Nemanich and Solin,[9] this peak is a result of the sum frequency of the two intense first-order bands occurring at 1590 and 1380 cm^{-1}.

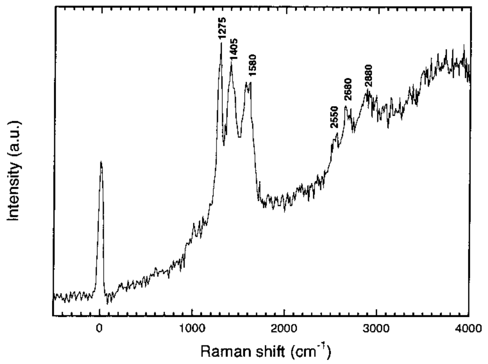

Figure 3. Single 25 ms integrated Raman spectrum of a Ag nanoparticle. This spectrum clearly demonstrates that the spectral features in the 2500−3000 cm^{-1} range result from linear combinations of the lower frequency bands.

In Figure 3, a single 25 ms exposure time SERS spectrum from a different Ag particle is shown. In comparison to the other spectra there is an additional line at 1275 cm^{-1} in the fundamental regime. It is interesting to note that lattice dynamics calculations of a single carbon sheet by Nemanich and Solin[9] and by Al-Jishi and Dresselhaus[12] predict three maxima (1581 cm^{-1}, 1360 cm^{-1}, and 1275 cm^{-1}) in the density of states, the lowest one right at the frequency of this line. Furthermore, the overtone at 2550 cm^{-1} and the combination at 2680 cm^{-1} = 1275 cm^{-1} + 1405 cm^{-1} in the high-energy part of the spectrum clearly show that this line must be associated with the fundamental in-plane mode of carbon sheets. Also part of the 2880 cm^{-1} band could be due to a combination with the 1580 cm^{-1} mode. This 1275 cm^{-1} line is missing in most previously reported ensemble spectra of graphite.[12] Here it is clearly visible as a sharp, intense peak. We want to note that very few Ag particles show this mode (see spectra in Figure 2) which explains the fact that it is not easily visible in an ensemble spectrum. The fact that this mode is missing in many spectra leads us to the following conclusions: (i) the appearance of this line must be associated with the finite size and, in addition, with the symmetry removal of the carbon nanocrystallite, (ii) the spectra where it is present must be dominated by one single crystallite which exhibits this mode. Further support of this single carbon domain claim lies in the fact that each sum frequency mode is generated by all possible combinations of the first-order peaks. If the first-order peaks were generated from more than one carbon domain, it would be expected that the modes would be different from one domain to another (since we have found this type of first-order spectrum to be quite rare).

In summary, we have observed surface-enhanced Raman scattering spectra of single carbon nanocrystals adsorbed to single silver nanoparticles. The time dependence of the movies clearly indicates that a few carbon nanocrystallites—and possibly just one—are being probed. Further, our results indicate that most Ag nanoparticles are SERS active and that the SERS enhancement renders the spectroscopic scattering cross-section to be similar to that of molecular fluorescence.

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