Probing the Structure of Single-Molecule Surface-Enhanced Raman Scattering Hot Spots

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The general application, however, of SMSERS requires synthetic or fabrication methods capable of routinely delivering substrates with single-molecule activity. Hitherto, pursuit of this goal has been hindered by a lack of knowledge about the specific nanostructures that give rise to SMSERS. As a result, the method for producing SMSERS active substrates, which relies on the salt induced aggregation of Ag nanoparticles, remains mostly unchanged since the original studies. These aggregated colloids are very heterogeneous, and only a fraction (∼1%) of them are SMSERS active.4 The few experiments making structural determinations of the SMSERS hot spots. To our knowledge this study is the most complete description of a nanostructure with confirmed single-molecule activity. This work both confirms existing speculations about the SMSERS active structures used atomic force microscopy1,5 and suggested that “hot” particles resulted from faceted particles or aggregation of two or more nanocrystals.

In this communication we report correlated high-resolution transmission electron microscope (HRTEM) images and optical spectra of nanoparticle structures that are confirmed to be single-molecule active. The derived structures are used as input for a series of electrodynamics calculations of the scattering spectra and local electric field enhancements, which elucidate the nature of the SMSERS hot spots. To our knowledge this study is the most complete description of a nanostructure with confirmed single-molecule activity. This work both confirms existing speculations about SMSERS and suggests simple structures that could serve as a template for the rational synthesis of SMSERS substrates.

The experiments described here build on methods outlined in a previous publication.3 Citrate reduced Ag colloids, after treatment with a mixture of Rhodamine 6G (R6G-d0) and R6G (R6G-d4), are aggregated with ~10 mM NaCl. Aliquots (10 μL) of the aggregated solution were drop-coated onto the surface of a copper TEM grid coated with a 50 nm layer of Formvar polymer and a 3 nm layer of amorphous carbon (Ted Pella). The substrate, after drying, was placed in a flow cell and purged with dry nitrogen during the optical measurements. SMSERS active particles were identified, and their Raman scattering (λex=532 nm) and dark field scattering spectra were recorded using a micro Raman setup. A dark field, wide field image of the particles or grid was recorded.

Figure 1. High-resolution TEM images of SMSERS active nanostructures. The simplest structures (a–c) are dimers of Ag nanocrystals. Structures consisting of three or more Ag nanocrystals are also often observed (d–f). SMSERS active nanostructures consisting of single Ag nanocrystals were not observed, suggesting they are rare or nonexistent.

The samples were then transferred to the TEM, where the active particle was identified through pattern matching.

The TEM images of representative SMSERS active particles are displayed in Figure 1. A wide range of structures are observed in the “hot” aggregates. The simplest structures are particle dimers, consisting of two Ag nanocrystals, while the most complicated contain many overlapping particles. As was observed previously,1 most of the hot particles are ~100 nm in size. We did not observe any SMSERS active structures that consisted of only one Ag nanocrystal. While this does not preclude their existence, it suggests that two or more particles are necessary for single-molecule activity.

Correlated spectra were recorded for each structure in Figure 1, and as observed previously by Brus and co-workers,7 the wavelength at which the dark field scattering spectrum is maximum bears no relation to the laser excitation frequency. Figure 2 displays the correlated optical spectra and TEM images for the particle in Figure 1a. This Ag nanocrystal dimer is the simplest single-molecule active structure observed to date. Based on the TEM image and depth profiling studies (resolution ~10 nm) we can approximate the structure in Figure 2 as a hemispherically capped rod and a sphere arranged in a “T” shaped geometry.

While the concept of electromagnetic hot spots in SERS predates the discovery of SMSERS,6,7 Brus and co-workers5,8 showed using polarization studies that hot spots formed at the junction of two nanoparticles likely play a major role in SERS. While model calculations9,10 indicate that SERS electromagnetic enhancement factors (EQM) can approach ~1011 in the junctions between nanoparticle dimers, calculations utilizing a structure that is known to be SMSERS active have not been performed previously. Therefore, using the structure in Figure 2a as input, we calculate the wavelength-dependent extinction efficiency (Qext) and local
previous studies of R6G SMSERS, was performed on resonance for R6G. The (resonance) Raman cross section of R6G, integrated over all observable modes with \( \lambda_{ex} = 514 \) nm, was recently measured by Shim, Stuart, and Mathies\(^{15} \) to be \( 2.3 \times 10^{-22} \) \( \text{cm}^2 \text{molecule}^{-1} \). Our DDA calculations indicate that the structure in Figure 3 can provide, conservatively, enhancements of \( 10^8 \) at 532 nm. If the observed cross section is a simple multiplication of the R6G resonance Raman cross section and the electromagnetic SERS enhancement factor, the resulting SMSERS cross section is \( 10^{-14} \) \( \text{cm}^2 \text{molecule}^{-1} \) which is in good agreement with the absolute cross sections of \( 10^{-14} \) \( \text{cm}^2 \text{molecule}^{-1} \) previously reported.\(^{1,8} \) With such large enhancements, subtle changes in the structure and adsorption geometry, as well as assumptions in the electrodynamics modeling, could easily lead to a factor of 10 difference in either direction; however, it appears that the combination of resonance Raman and electromagnetic hot spots accounts for most of the observed SMSERS enhancement. Lastly, our calculations indicate that the location of the hot spot at 532 nm is near, but not at the intersection of the two particles, thus confirming the idea that SMSERS hot spots occur near the particle–particle junction.

In conclusion, we present here a detailed study of the specific nanoparticle structures that give rise to SMSERS. A variety of structures are observed, but the simplest are dimer structures. Our electrodynamics calculations suggest the enhancement factor in SMSERS is consistent with a combination of molecular resonance enhancement and electromagnetic enhancement. In addition, although the electromagnetic enhancement peaks near the plasmon maximum \( \approx 470 \) nm, it drops off slowly as the wavelength shifts red. This rationalizes the absence of correlation between maxima in the Rayleigh scattering spectra and excitation wavelength in SMSERS. Lastly, the structures observed here suggest simple templates for the rational synthesis of high density SMSERS active substrates.

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References

(13) Use of 1 nm dipole spacing in this work leads to an evaluation of the fields 0.5 nm from the surface rather than at the surface. A discussion is presented in Hao, E.; Schatz, G. C. J. Chem. Phys. 2000, 120 (1), 357–366.

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