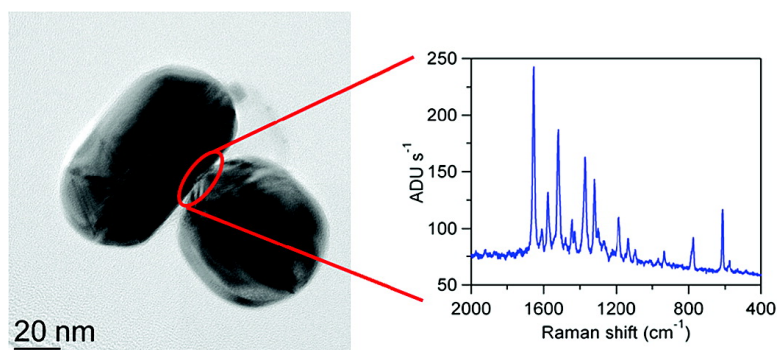


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## Probing the Structure of Single-Molecule Surface-Enhanced Raman Scattering Hot Spots

Jon P. Camden,<sup>†</sup> Jon A. Dieringer,<sup>†</sup> Yingmin Wang,<sup>‡</sup> David J. Masiello,<sup>†</sup> Lawrence D. Marks,<sup>‡</sup> George C. Schatz,<sup>\*,†</sup> and Richard P. Van Duyne<sup>\*,†</sup>

Department of Chemistry, Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208-3113

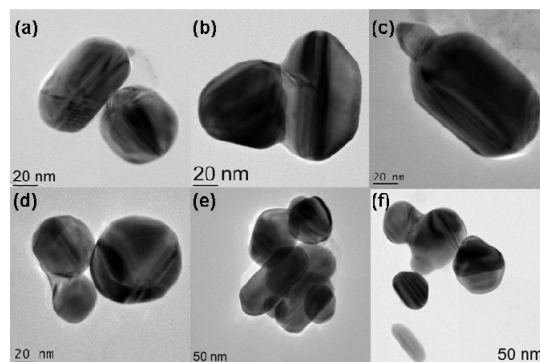
Received July 3, 2008; E-mail: schatz@chem.northwestern.edu; vanduyne@northwestern.edu

Single-molecule surface-enhanced Raman scattering (SMSERS), first observed by Nie and Emory<sup>1</sup> and Kneipp et al.<sup>2</sup> in 1997, provides one of the few methods available for obtaining the vibrational spectrum of a single molecule. It was immediately recognized that this powerful combination of single-molecule sensitivity and spectroscopic fingerprinting could provide insight into a wide range of chemical and biological systems. In the decade since its discovery, many aspects of SMSERS have been elucidated and its single-molecule character, sometimes in question, has now been well established.<sup>3</sup>

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.<sup>4</sup> The few experiments making structural determinations of the SMSERS active structures used atomic force microscopy<sup>1,5</sup> 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 electrodynamic 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.<sup>3</sup> Citrate reduced Ag colloids, after treatment with a mixture of Rhodamine 6G (R6G-d<sub>0</sub>) and R6G (R6G-d<sub>4</sub>), 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 2–3 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 ( $\lambda_{\text{ex}}=532$  nm) and dark field scattering spectra were recorded using a micro Raman setup. A dark field, wide field image of the particles and 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.

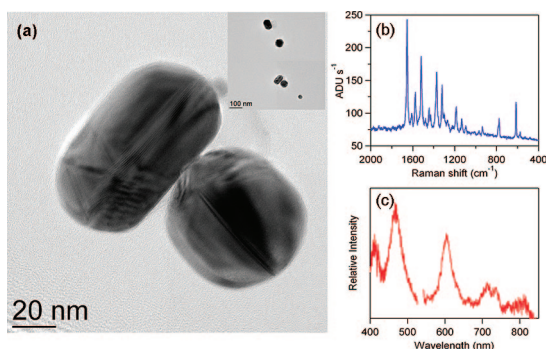
The TEM images of representative SMSERS active particles are displayed in Figure 1. A wide range of structures are observed in the “hot” aggregates. The simplest structures are particle dimers, consisting of two Ag nanocrystals, while the most complicated contain many overlapping particles. As was observed previously,<sup>1</sup> 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,<sup>5</sup> 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.

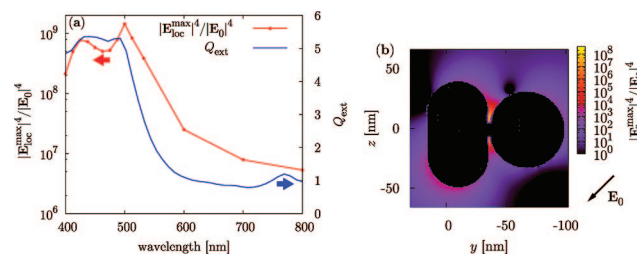
While the concept of electromagnetic hot spots in SERS predated the discovery of SMSERS,<sup>6,7</sup> Brus and co-workers<sup>5,8</sup> showed using polarization studies that hot spots formed at the junction of two nanoparticles likely play a major role in SMSERS. While model calculations<sup>9,10</sup> indicate that SERS electromagnetic enhancement factors ( $E_{\text{EM}}$ ) can approach  $\sim 10^{11}$  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 ( $Q_{\text{ext}}$ ) and local

<sup>†</sup> Department of Chemistry.

<sup>‡</sup> Department of Materials Science and Engineering.



**Figure 2.** Correlated TEM (a), Raman scattering (b), and dark field scattering spectrum (c) of a single-molecule SERS active structure.



**Figure 3.** Optical properties of the SMSERS active structure in Figure 2a obtained from 3D calculations using DDA. The structure is approximated as a T-shaped dimer consisting of a sphere and a hemispherically capped rod that just touch (0 nm separation). (a) Extinction efficiency (blue line) and maximum SERS enhancement  $E_{EM}$ , calculated as  $|E_{loc}^{max}|^4/|E_0|^4$ , (red line) for each wavelength. (b) Contour plot of  $E_{EM}$  at the plane  $x = -4$  nm, where the maximum value of  $E_{EM} = 3.9 \times 10^8$  at 532 nm is observed. For reference the plane  $x = 0$  is defined as where two Ag nanocrystals touch, indicating the hot spot is localized at the cusp between the particles.

values of  $E_{EM}$ , calculated as  $|E_{loc}^{max}|^4/|E_0|^4$  using the discrete-dipole approximation (DDA).<sup>11</sup> The effects of polarization, choice of dielectric constant, and dimer spacing, i.e. the separation between the sphere and rod, were all considered. Variation of these parameters causes subtle changes in the extinction spectra and local field enhancements but overall leads to similar results; therefore, for simplicity of presentation, we concentrate on only one polarization using the dielectric constants from Palik.<sup>12</sup>

Results of our DDA calculations are presented in Figure 3. The scattering spectrum in Figure 3a reproduces the main feature at  $\sim 470$  nm observed in Figure 2. The additional feature at  $\sim 600$  nm in the experiment is likely the result of another particle within the diffraction limit (inset in Figure 2a). Figure 3 also shows the maximum calculated value of  $|E_{loc}^{max}|^4/|E_0|^4$  as a function of wavelength. The largest calculated enhancements are observed at 500 nm and correspond to  $E_{EM} = 1.4 \times 10^9$ . This calculated enhancement refers to touching particles and may be a lower bound;<sup>13</sup> enhancements that are a factor of  $\sim 10$  higher are obtained if the particles are allowed to be separated by 1 nm. At the wavelength of our experiments,  $\lambda = 532$  nm, this structure still provides an electromagnetic hot spot with  $E_{EM} = 3.9 \times 10^8$  even though this wavelength is well off the peak of the extinction spectrum. While the largest calculated values of  $E_{EM}$  occur at the maximum of the Ag nanocrystal dimer extinction spectrum, the peak  $E_{EM}$  remains greater than  $10^7$  across the visible portion of the spectrum. This observation is likely one reason why the peak in the nanostructure extinction spectrum is not correlated with the laser excitation frequency in SMSERS.

Unfortunately, there has been considerable confusion in the literature about the enhancement factors required for SMSERS as recently discussed by Etchegoin et al.<sup>14</sup> Our study, similar to

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<sup>15</sup> to be  $2.3 \times 10^{-22}$  cm<sup>2</sup> molecule<sup>-1</sup>. 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  $10^{-14}$  cm<sup>2</sup> molecule<sup>-1</sup> which is in good agreement with the absolute cross sections of  $10^{-14}$  cm<sup>2</sup> molecule<sup>-1</sup> previously reported.<sup>1,8</sup> 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 ( $\sim 470$  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

- (1) Nie, S.; Emory, S. R. *Science* **1997**, *275* (5303), 1102–1106.
- (2) Kneipp, K.; Wang, Y.; Kneipp, H.; Perelman, L. T.; Itzkan, I.; Dasari, R. R.; Feld, M. S. *Phys. Rev. Lett.* **1997**, *78* (9), 1667–1670.
- (3) Dieringer, J. A.; Lettan, R. B. II; Scheidt, K. A.; Van Duyne, R. P. *J. Am. Chem. Soc.* **2007**, *129*, 16249–16256.
- (4) Doering, W. E.; Nie, S. M. *J. Phys. Chem. B* **2002**, *106* (2), 311–317.
- (5) Michaels, A. M.; Jiang, J.; Brus, L. *J. Phys. Chem. B* **2000**, *104* (50), 11965–11971.
- (6) Gersten, J.; Nitzan, A. *J. Chem. Phys.* **1980**, *73* (7), 3023–3037.
- (7) Metiu, H.; Das, P. *Annu. Rev. Phys. Chem.* **1984**, *35*, 507–536.
- (8) Michaels, A. M.; Nirmal, M.; Brus, L. E. *J. Am. Chem. Soc.* **1999**, *121* (43), 9932–9939.
- (9) García-Vidal, F. J.; Pendry, J. B. *Phys. Rev. Lett.* **1996**, *77* (6), 1163.
- (10) Xu, H. X.; Aizpurua, J.; Kall, M.; Apell, P. *Phys. Rev. E* **2000**, *62* (3), 4318–4324.
- (11) Draine, B. T.; Flatau, P. J. *J. Opt. Soc. Am. A* **1994**, *11* (4), 1491–1499.
- (12) Palik, E. D. *Handbook of Optical Constants of Solids*; Academic: New York, 1985.
- (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.* **2004**, *120* (1), 357–366.
- (14) LeRu, E. C.; Blackie, E.; Meyer, M.; Etchegoin, P. G. *J. Phys. Chem. C* **2007**, *111* (37), 13794–13803.
- (15) Shim, S.; Stuart, C. M.; Mathies, R. A. *ChemPhysChem* **2008**, *9* (5), 697–699.

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