Direct Observation of Size-Dependent Optical Enhancement in Single Metal Nanoparticles

Steven R. Emory, William E. Haskins, and Shuming Nie*

Department of Chemistry, Indiana University
Bloomington, Indiana 47405

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Metal and semiconductor particles on the nanometer scale have unique optical, electronic, and structural properties that are not available in either isolated molecules or bulk solids.[1] These properties are currently under intense study for potential use in microelectronics, quantum dot lasers, chemical sensors, data storage, and a host of other applications. However, current research is based mainly on population-averaged measurements, in which a large number of nanoparticles are studied and their average responses are recorded. These experiments yield only population-averaged results and not the intrinsic or fundamental properties of the nanomaterial. In this paper, we report the direct measurement of size-tunable optical properties in single Ag nanoparticles. Ultrasensitive spectroscopy at the single-particle level overcomes the problem of inhomogeneous broadening and should provide new insights into the optical and electrical properties of nanostructured materials.[2−5]

We have used surface-enhanced Raman scattering (SERS) and Ag colloidal nanoparticles to examine the relationship between optical excitation wavelength and particle size. Figure 1 shows the surface-enhanced Raman spectra of rhodamine 6G (R6G) obtained from three different Ag nanoparticles. These particles were identified from a heterogeneous colloidal population by wide-field screening at 488, 568, and 647 nm, respectively.[6] Each particle exhibits maximum surface enhancement at the screening laser wavelength and a relatively narrow excitation profile (compared to colloidal nanoparticle aggregates).[7] This wavelength-dependent behavior is not observed in bulk SERS studies because of the large variations in particle size, shape, and surface defects.[8]

Correlated optical and morphological studies reveal that the optically active nanoparticles identified at different wavelengths have dramatically different sizes. Figure 1 (lower part) shows tapping-mode AFM images of the three nanoparticles mentioned above. The intrinsic enhancement factors on these optically "hot" particles are as large as $10^{14}-10^{15}$, much higher than those derived from bulk measurements.[9,10] To reach a general consensus, we have examined a large number (>50) of colloidal nanoparticles with an integrated optical and atomic force microscope. The particle size is based on height values because tip convolution makes lateral measurements less accurate.[11] The results show that the 488-nm-excited particles have an average size (diameter) of 70 nm with a standard deviation of 6 nm and that the 568-nm-excited particles have an average size of 140 nm with a standard deviation of 9 nm.[12] For efficient excitation at 647 nm, the nanoparticles are about 190−200 nm with a standard deviation of 20 nm. This finding is in agreement with the previous report that the "hot" nanoparticles at 514.5-nm excitation have a narrow size range of 80−100 nm.[9] For the SERS-active particles, the relationship between particle size and excitation wavelength is found to be approximately linear (Figure 2). However, the use of R6G as a probe molecule is complicated by resonance Raman enhancement.[13] To overcome this problem, we have studied a number of analyte molecules that have no electronic transitions in the visible, such as pyridine, bipyrdine, and hydroxykynurenine. A similar particle size/wavelength relationship is found for these nonresonant molecules.

These optical and AFM data strongly support the resonant excitation of free electrons (surface plasmons) in small metal particles.[14] The electromagnetic field theory developed by Schatz and co-workers shows that the wavelength dependence on particle size is roughly linear at large sizes and that the slope is a strong function of particle shape.[15] Our experimentally determined slope is larger than that calculated for 1:1 aspect ratio but smaller than that for 2:1 ratio. Indeed, detailed TEM and AFM measurements reveal that the optically active Ag particles have a typical aspect ratio of 1.5:1.

A further finding is that the 70-nm particles emit green light and the 140-nm particles emit red/orange light when excited at multiple wavelengths. Figure 3 shows a multicolor Raman image obtained from Ag nanoparticles excited with a mercury lamp at 490 and 570 nm.[16] The probe molecule is *trans*-1,2-bis(4-pyridyl)ethylene, which is not resonance-enhanced at these wavelengths. This multicolor phenomenon occurs because the 490-nm-excited particles emit Raman-shifted photons in the green and the 570-nm-excited particles emit Raman photons in the orange and red regions. It is surprising, however, that a third type of nanoparticle is observed which emit "yellow" light. Correlated optical and AFM measurements show that these particles are either single nanoparticles with intermediate sizes (∼115 nm) or nanoaggregates consisting of two to three particles. Such nanostructures can be excited at both 490 and 570 nm and emit Stokes-shifted light in the green and the red. The superposition of green and red yields the composite color of yellow. This type of particle is still much smaller in size than the light wavelength and is detected as diffraction-limited spots in far-field optical microscopy. Combined with single-particle spectroscopy and tapping-mode AFM, this multicolor screening method provides a powerful means for high-speed screening and characterization of novel nanoparticles and nanoaggregates.

In conclusion, we have directly measured the size-tunable optical properties in spatially isolated, single metal nanoparticles.

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* To whom correspondence should be addressed. E-mail: nie@indiana.edu

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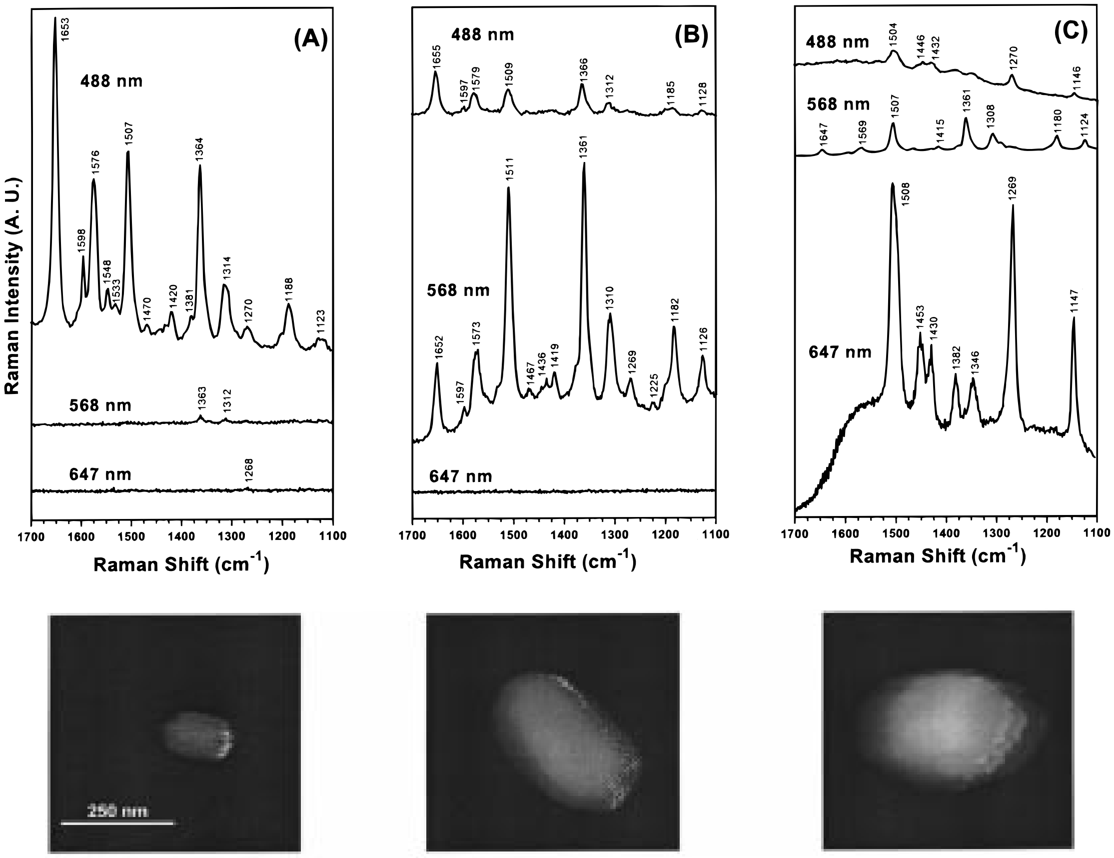

Figure 1. Correlated surface-enhanced Raman spectra and tapping-mode AFM images obtained from spatially isolated, single Ag nanoparticles. These particles were selected by wide-field screening for maximum enhancement at (A) 488 nm, (B) 567 nm, and (C) 647 nm, respectively. The Raman spectra were acquired sequentially at each excitation wavelength with a constant laser power of 20 μW and a data integration time of 5 s.

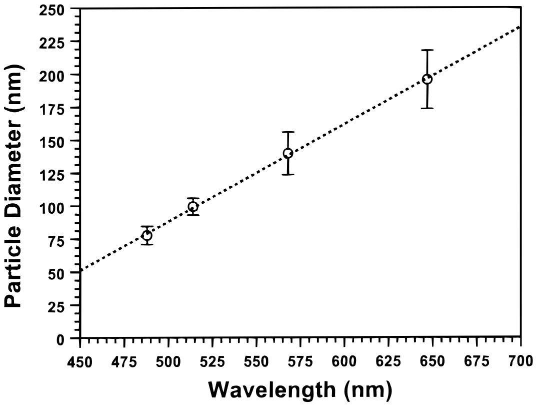

Figure 2. Plot of particle size as a function of excitation wavelength. Particle sizes are the average values of five or more nanoparticles measured at each wavelength. The error bars indicate size variations at three standard deviations.

The results show that the single-particle excitation profile is relatively narrow and that an approximate linear relationship exists between the optical excitation wavelength and the particle size. This fundamental insight should help the rational design of nanostructured materials (e.g., SERS-active substrates)[17] and stimulate further experimental and theoretical work aimed at understanding the mechanisms of surface optical enhancement. This work also opens new possibilities in searching for unusual properties in semiconductor quantum dots and organic nanostructures.

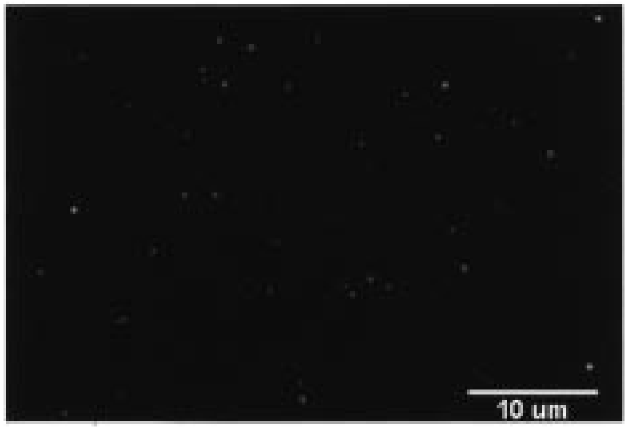

Figure 3. Multicolor Raman image of Ag nanoparticles excited with a mercury lamp at 490 and 570 nm. The probe molecule is bis(4-pyridyl)-ethylene (BPE). The green, red, and yellow signals correspond to 70-nm particles (excited at 490 nm), 140-nm particles (excited at 570 nm), and intermediate-sized particles or nanoaggregates (excited at both 490 and 570 nm).

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