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Creating Hot Nanoparticle Pairs for Surface-Enhanced Raman Spectroscopy through Optical Manipulation

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ABSTRACT

We use optical tweezers to move single silver nanoparticles into near-field contact with immobilized particles, forming isolated surface-enhanced Raman spectroscopy (SERS) active Ag particle dimers. The surface-averaged SERS intensity increases by a factor ~20 upon dimerization. Electrodynamics calculations indicate that the final approach between the particles is due to "optical binding". The described methodology may facilitate controlled single molecule SERS analysis.

Nanoparticles composed of noble metals exhibit an enhanced optical interaction with visible light due to the resonant excitation of collective electron oscillations, so-called localized surface plasmons (LSP's),[1] which are important for the development of novel nanoscopic bio/chemosensors.[2] However, LSP excitation not only renders the particle a specific color—blue to green, in the case of spherical silver particles—but it also leads to enhanced optical fields near the nanoparticle surface. This phenomenon is the basis for surface-enhanced Raman scattering (SERS),[3] which in some cases allows for vibrational spectroscopy down to the single molecule detection limit.[4,5] Isolated nanoparticles usually yield a weak SERS response compared to aggregates, because the latter enables additional strong field enhancement in the gap regions between the particles.[5,6] Consequently, much recent effort have been directed at developing SERS substrates based on closely spaced nanoparticles.[7−10] However, the controlled creation of individual nanoparticle pairs, of the kind needed for single molecule analysis, has remained a challenge. In this work, we create such pairs at will using optical manipulation.

Optical manipulation is usually achieved using so-called optical tweezers, i.e., a single tightly focused laser beam that can trap microscopic dielectric objects due to high electric field gradient forces.[11] Metal particles are difficult to trap, due to their high reflectivity, but it has been shown that optical trapping of noble metal nanoparticles is indeed possible, provided that the laser frequency is far enough below the LSP resonance frequency.[12−14] The optical tweezers used here are built around a Raman microscope configuration,[14] using near-infrared (NIR) laser light ($\lambda =$

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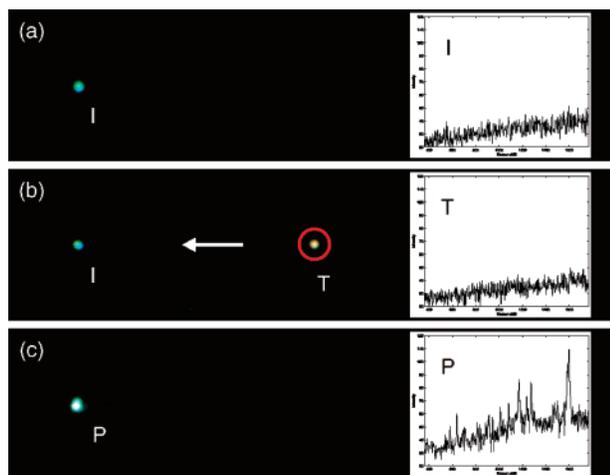
Figure 1. Dark-field images of trapped and immobilized Ag nanoparticles. (a) SERS spectrum from a single immobilized particle (I) shows no signal. (b) An optically trapped particle (T), without SERS signal, is moved toward the immobilized one. (c) When brought into near-field contact, the particle pair (P) shows a strongly enhanced SERS signal.

830 nm, $P = 50$ mW) for trapping and visible laser light ($\lambda = 514.5$ nm, $P = 0.5$ mW) for Raman excitation in a backscattering geometry. A thin sample cell allows for use of an oil immersion transmitted dark-field (DF) condenser for digital photography and an oil immersion microscope objective with high numerical aperture for trapping, SERS excitation and signal collection. A stable sodium citrate silver colloid was prepared and diluted down to ~5 pM. The nanoparticles in the solution are roughly spherical and with an average diameter of 40 nm. We used thiophenol, with a final sample concentration of 10 μM, as our probe molecule. The thiol group forms a specific and strong bond with silver, which results in highly reproducible and stable SERS spectra.

With a low particle concentration in the sample cell and a trapping laser power tuned down to the extent that trapping can just be achieved, we avoid ending up with a large number of particles in the trapping volume. In this way, controlled manipulation of single particles in two dimensions could be performed and visualized through DF microscopy. In order to investigate the influence of interparticle coupling on the SERS signal, we first recorded the SERS spectrum from a single particle stuck on the sample cell surface. We then trapped a diffusing particle and brought it into near-field contact with the immobilized particle, after which the "aggregate" SERS spectrum was recorded. Figure 1 illustrates a typical measurement. In the dark-field microscope, the particles appear as diffraction-limited spots with a color determined by their LSP resonance wavelength. As seen in Figure 1a, the immobilized particle (I) is green, and it can therefore be expected to be SERS active for the Raman excitation wavelength used. The trapped particle (T) is yellow and should also be SERS active. However, neither of these particles exhibits a SERS signal above the noise level. As can be seen in Figure 1c, a clear thiophenol spectrum only appears when the optically trapped particle is moved to the same position as the immobilized one. We have thus created a SERS-active silver particle dimer through optical manipu-
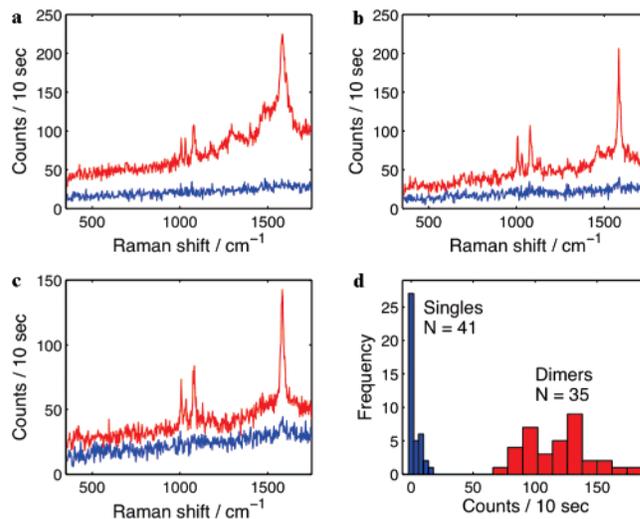
Figure 2. (a), (b), and (c) Three examples of SERS measurements from a single immobilized particle (lower trace in each figure) at the surface and the following spectra from the same spot after a diffusing particle has been trapped and moved onto the immobilized one (upper trace in each figure). (d) A histogram of the SERS intensities recorded for 35 different dimers formed through optical manipulation and 41 different single imobilized particles. The bin sizes for the dimers and the single particles are 16 and 2 counts per 10 s integration, respectively, and the lowest bin includes particles that did not exhibit any measurable signal above the noise level.

lation. Figure 2a−c gives three more examples of optical "paring" of nanoparticles. Here we removed the optics needed for DF photography in order to improve the signal-to-noise ratio. In all cases, we observe a very large increase in the SERS signal from the optically created particles pairs compared to the single particle spectra. These measurements were relatively straightforward to reproduce, and the intensities from both the single particles and the particle pairs were always in the range of the three examples displayed for the same experimental conditions. Figure 2d shows a histogram of the observed signals from 35 dimers formed through optical manipulation and 41 single particles immobilized on the cover glass. The average SERS efficiency amplification due to dimerization is found to be ~22 times per particle. This is similar to the signal increase seen for extended SERS substrates due to particle coupling.[7−10] However, we should note that the SERS intensity represents an average over the metal surface—the enhancement within the interparticle region, which is the relevant factor for single molecule analysis, should be orders-of-magnitude higher.[5,6]

The observation that two particles that are brought together in a laser trap produce a much stronger SERS spectrum than the sum of two individual particle spectra might not be surprising, considering the aforementioned importance of aggregation in SERS. However, if one consider the actual length scales involved in the trapping and interparticle-coupling effects, the result is not obvious. The interparticle-coupling effect in SERS is an optical near-field phenomenon that requires the particles to be within at least a particle radius (~20 nm for the particles considered here) from each other. The size of the trap, on the other hand, is of the order of the beam waist (~1 μm). Moreover, the laser power used for
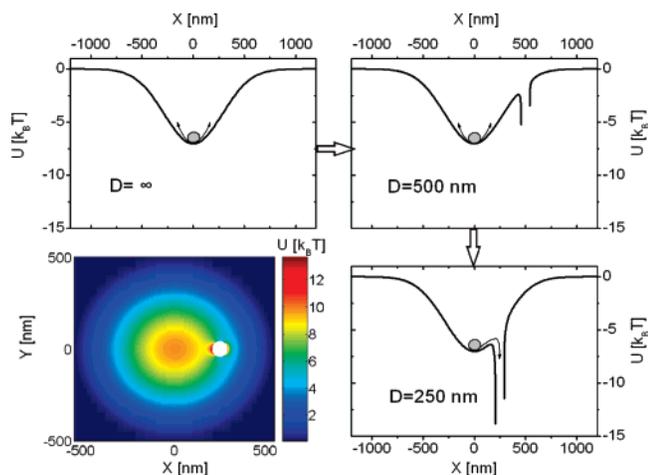
Figure 3. Spatial variation of the optical potential experienced by a mobile 40 nm Ag particle in a focused Gaussian beam ($\lambda = 830$ nm, $P = 50$ mW, beam-waist radius $w_0 = 0.5\ \mu$m) for different distances D between the laser focus and a second immobilized 40 nm Ag particle. The potential U in units of k_BT ($T = 300$ K) is calculated in the focal plane of the laser ($z = 0$) along the direction of the incident polarization (x-direction). The color map shows the potential in the xy-plane for $D = 250$ nm.

the manipulation experiment above was reduced to a level where the particles could just be trapped, implying that the thermal particle movement within the trap should be significant, and our precision in positioning particles is, at best, diffraction limited. Taken together, it is difficult to see how a significant SERS increase can occur in the trap without the presence of an additional "aggregating" force that brings the particles into the near-field coupling regime. However, such a force does exist, due to the optical potential created by the induced multipolar fields from the particles.[15,16] In brief, if both particles are aligned parallel to the incident polarization, the local intensity is highest in the interparticle region, resulting in a gradient force that pulls the particles together, similar to the so-called "optical binding" effect that has been demonstrated experimentally for micrometer-sized dielectric particles.[17]

In Figure 3, we show an electrodynamics simulation of the optical binding phenomenon for two 40 nm Ag particles in an illumination configuration that mimics our experimental trapping setup. The first figure shows the potential well experienced by the trapped particle when it is far away from the particle stuck on the surface. We then redo the calculation for the cases when the distance D between the laser focus and the immobilized particle is 500 and 250 nm. As can be seen in the figure, the presence of the immobilized particle strongly modifies the potential energy surface experienced by the mobile particle, producing a second deep potential well corresponding to optical binding between the two

particles. For $D = 250$ nm, the barrier between the two minima is clearly smaller than the thermal particle energy. Thus, once the optically trapped particle is within this distance from the immobilized particle, it has a high probability to jump into the near-field coupling zone, resulting in a strong increase in the SERS intensity. While a definite proof would require additional high-resolution imaging, the data in Figures 1 and 2 constitute a strong experimental indication for this kind of optically induced aggregation of metal nanoparticles.

In summary, we have utilized optical tweezers technology to pair up individual silver nanoparticles for surface-enhanced Raman spectroscopy, a methodology that may pave the way for controlled single molecule Raman analysis. Theoretical considerations indicate that optical binding enables the final approach of the two particles within the micrometer-sized optical trap.

Supporting Information Available: Details of the experimental procedure, materials and equipment, and the computational method. This material is available free of charge via the Internet at http://pubs.acs.org.

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