Detection of plasmon-enhanced luminescence fields from an optically manipulated pair of partially metal covered dielectric spheres

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Using optical tweezers combined with luminescence measurements we detected the optical field around two optically trapped silica microspheres partially covered by metal. By monitoring the luminescence of rhodamine 6G we were able to observe an increase of the local field intensity owing to the coupling of the local surface plasmons at the surfaces of two spheres. © 2008 Optical Society of America

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The enhancement of field intensity due to local plasmon resonances near nanoscopically textured metal structures leads to many fascinating optical effects. One of them is the surface-enhanced Raman scattering (SERS), which has been established as a powerful spectroscopic technique for chemical analysis of molecules, combining high sensitivity with structural information [1].

One way to further increase this field enhancement is the use of closely spaced nanoparticles [2–4]. An optical trap created by a strongly focused optical beam could be a promising method to control the creation of individual nanoparticle pairs in a liquid medium. However, for tens of nanometer-sized metal particles the stable 3D trapping is possible only for a short time [2,3,5–7]. Recently, silica spheres partially covered with metal (SPCM) were used for SERS [8]. The spheres were sufficiently transparent to allow light to refract through them, enabling the optical trapping while the presence of metal islands provided the SERS.

While prior publications have focused on single SPCM one may also expect stronger resonances by approaching such an optically trapped sphere to a metal surface or to another SPCM realizing an efficient coupling between plasmonic modes of two metal surfaces. However, the optical trapping is always accompanied by Brownian motion. A question arises whether it is possible to observe an average enhancement of the optical field between two adjacent optically trapped SPCMs by their continuous random translational and rotational motion.

We studied experimentally the distribution of the field between two optically manipulated SPCMs using the luminescence of rhodamine 6G (R6G) molecules as a probe of the local field intensity. We prepared SPCM through the colloidal attachment of silver to the surface of 2.0 μm silica beads covered with a self-assembling monolayer. The transmission spectrum of a solution of such spheres reveals a dip near 450 nm, indicating the presence of silver colloids. As a sample, an aqueous solution was prepared that contained a low (1 g/L) concentration of SPCMs and R6G molecules.

To create two traps with a variable distance between their centers we used the setup shown in Fig. 1(a). A beam from a 980 nm laser passed consequently through an acousto-optic modulator and a deflector. A system of two lenses permits conjugation of the output plane of the deflector and the input pupil of a $100\times$(NA=1.3) objective that focuses the beam inside a custom made chamber. Using a square modulation signal for the deflector with 10 kHz switching frequency we produced two traps with a separation that can be changed at 10 nm steps.

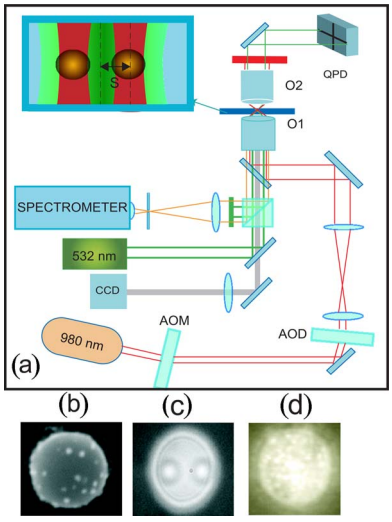

Fig. 1. (Color online) (a) Experimental setup where the inset shows the sample with SPCM trapped by two 985 nm beams (gray) and illuminated by the 532 nm beam (black). s is the separation distance measured between the center of of the sphere and the center of the excitation 532 nm beam. (b) Electron microscope image of a 2 μm SPCM, (c) two trapped 2 μm spheres seen after the pinhole PH of the confocal system, (d) hot spots at the surface of the SPCM.

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To excite the luminescence of R6G molecules a second cw 532 nm beam was introduced through a dichroic mirror along with the trapping beam. We estimated the diameter of this beam at the focal plane to be around 1 μm. The luminescence emission of the R6G molecules was collected by the trapping objective and then passed through a confocal system (300 μm confocal pinhole) before arriving at a spectrometer. We analyzed the probe position fluctuations due to Brownian motion by a position detector. Its calibration was based on the established theory of Brownian motion of a particle in a confining potential [9]. For this measurement the intensity of the 532 nm beam was reduced greatly so that it did not interfere with the 980 nm trapping. The forward scattered 532 nm light from a sphere trapped by the 980 nm beam was collected by a 40$\times$objective (O_2) and passed to a quadrant photodetector (QPD).

Figure 1(b) is a scanning electron microscopy (SEM) image of a typical sphere after the silver colloid attachment. In Fig. 1(c), the image of two trapped spheres after the confocal pinhole is shown along with a magnified image [Fig. 1(d)] of a single sphere. To get these images the excitation beam before the pinhole was cut by a filter, hence, the images were produced by the luminescence emitted by the R6G molecules near to, or adsorbed on, the metal areas of the probe surface. One can distinguish "hot" areas on the sphere surface with enhanced field intensity that generate a strong luminescence response. We estimate the confocal volume for the luminescence signal to be 3 μm^3.

Figure 2 shows the difference spectra, i.e., the spectra obtained minus the spectrum measured without a trapped sphere in the pump beam. To avoid bleaching effects, measurements were done with the incident 532 nm beam power at 20 μW, with a 50 s acquisition time for each spectrum. The integral luminescence was obtained by integrating the difference spectrum between 560 and 680 nm, which is the observed range of fluorescence R6G.

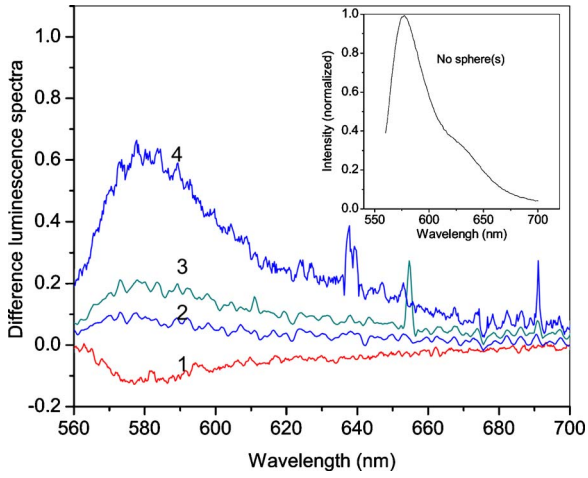

Fig. 2. (Color online) Difference spectra obtained with (1) an uncoated silica 2 μm sphere in the center of the 532 nm beam, (2) a single SPCM in the center of the 532 nm beam, and (3) and (4) a pair of SPCMs located symmetrically relative to the center of the 532 nm beam with two separation distances. The inset shows the normalized luminescence spectrum when no spheres are in the confocal volume.

The plain dielectric sphere caused a decrease of the luminescence intensity compared with the reference, because the R6G molecules were expelled from the confocal volume with the sphere in the center. Conversely, the luminescence signal for the single SPCM was higher, indicating the field enhancement. When two SPCMs were introduced into the excitation beam, the degree of enhancement was dependent on the distance between the spheres.

In Fig. 3 we examined the integral luminescence for two experiments: (1) a single SPCM moves through the 532 nm beam and (2) the distance between two SPCMs that are held symmetrically about the 532 nm beam center is varied. We also measured the integral luminescence with a single plain dielectric sphere in the excitation beam center. With a single SPCM the signal grows as the sphere approaches the pump beam center and is always greater than the luminescence signal without the sphere. However, when the sphere is at the pump center the signal decreases to that obtained with the plain dielectric sphere at the same position.

When a pair of trapped spheres is placed symmetrically about the pump beam center the enhancement is much stronger and grows almost exponentially until the separation distance (s) defined in the inset in Fig. 1(a) approaches 1 μm, the point at which the spheres touch each. We measured also a histogram of the sphere position variance (the inset in Fig. 3). The amplitude of displacement of the sphere from the trap center ranges up to 100 nm, which is the minimal value that we could achieve with the trapping beam power used. Since the local field enhancement between two coupled metal nanoparticles var-

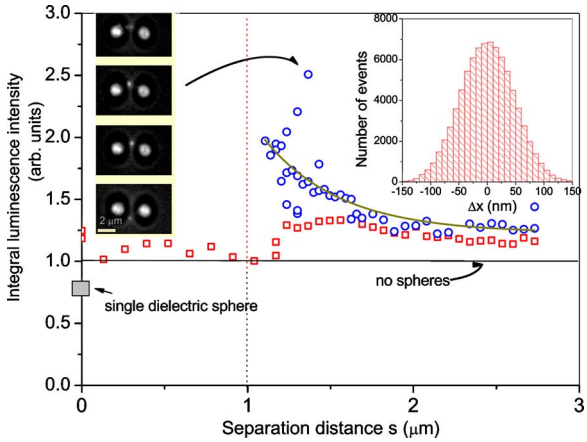

Fig. 3. (Color online) Integral luminescence signal versus distance for a single SPCM moving through the excitation beam (open squares) and for two SPCMs approaching each other symmetrically about the 532 nm beam axis (open circles). Insets, right, a histogram of the sphere position; left, frames of a movie showing fluctuations of the luminescence intensity. All values are normalized to the integral luminescence measured without spheres in the excitation beam (shown as a solid curve). A solid square shows the signal when a single plain dielectric sphere is trapped in the center of the 532 nm beam. The vertical dashed line shows the separation distance when the spheres touch.

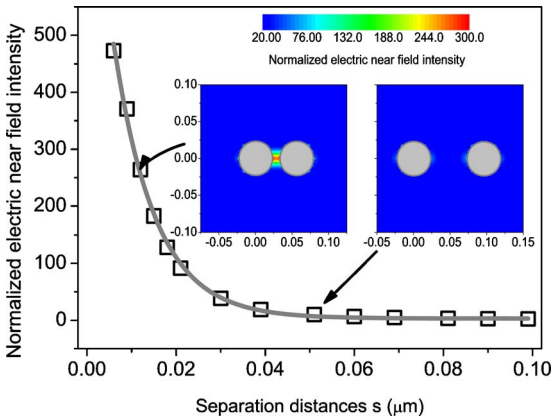

Fig. 4. (Color online) Field intensity in the midpoint between the two particles versus the separation distance. The insets show the field intensity distribution between nanospheres calculated for two separation distances. In the calculation an incident plane wave at a wavelength of 532 nm was used with polarization along the line that unites the centers of the particles.

ies strongly at this length [2,3], the large fluctuations of luminescence intensity, which are observed at a separation distance of 500 nm and less, are certainly understandable. We did not observe considerable fluctuations of the luminescence intensity with one SPCM in the trap. The sphere position variance is not enough to remove the sphere from the pump beam center so that the average pump intensity at the sphere surface is kept constant, thus allowing the average enhancement of the luminescence signal to remain stable. Analyzing frames [Fig. 3 (left inset)] of a video obtained after the pinhole we observed a random appearance of strong flashes of luminescence connecting the sphere surfaces. The origin of flashes were located in random places of the sphere surfaces, and it is believed that the flashes are due to the random field enhancement between the metal areas at two spheres when Brownian motion approaches them up to nanometer distances.

Using the Green dyadic method [10] we numerically simulated the near field between two cylinders with a diameter of 45 nm and 21 nm of height, which are the average sizes of the metal areas observed at the sphere surfaces [Fig. 1(b)]. This formalism provides a self-consistent resolution of the Maxwell equations, accounting for the multipolar response of metallic nanoparticles. The results are presented in Fig. 4. As seen, the field intensity grows, as expected, by approaching the particles to each other, which is in agreement with the experimental observation.

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