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ORIGINAL PAPER

Local Field Spectroscopy of Metal Dimers by TPL Microscopy

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Abstract We report on two-photon photoluminescence (TPL) spectroscopy on metal dimers made of two gold nanoparticles separated by subwavelength distances. A direct comparison with far-field scattering measurements shows that TPL provides additional data on the structure modes of major importance for their use in surface-enhanced Raman scattering, enhanced fluorescence, and sensing.

Keywords Plasmons · Two-photon photoluminescence · Near-field optics

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Introduction

Optimizing the interaction of light with nanometer volumes of matter is a major objective of nanophotonics that may contribute to the elaboration of future nanodevices. For this purpose, the confinement of light fields down to dimensions much smaller than the incident wavelength is highly desired together with a high field magnitude. Metallic nanostructures sustaining localized surface plasmon modes have shown to be well suitable for fulfilling these two requirements. In particular, dimer geometries formed by two closely spaced nanoparticles provide dramatic field enhancement and confinement volume in their gap [1] (Figure 1).

The fabrication of such nanostructures, although critical, is now rendered accessible by standard e-beam lithography techniques. A remaining major issue is their optical characterization with light field confinement at the edge of maximum resolution in near-field optical microscopy [2]. Lately, several works have shown the pertinence of two-photon photoluminescence (TPL) microscopy for probing the local optical response of resonant gold nanostructures [3]. Because of the nonlinear dependence of its excitation, the TPL signal is proportional to the fourth power of the electromagnetic field in the metal. In the dimer geometry, this provides a good approximation to the maximum field values in the air gap between the two particles. Previous studies have shown that the field enhancement factor at resonance can be quantitatively estimated in good agreement with theoretical predictions [4,5].

In applications such as surface-enhanced Raman scattering and enhanced fluorescence, where such *hot spots* are of interest, molecules adsorbed at the metal surface or close from it mainly respond to the electric near-field intensity. To predict their response, it is desired to look at the near-field spectroscopy of the metal host rather than its (far-field) scattering or extinction spectroscopy. This becomes even more crucial when the metallic system is large enough to experience some significant retardation effects. In that case, indeed, the near-field spectroscopy may display important differences with the far-field [6].

To the best of our knowledge, the work we present is the first experimental comparison between far-field and near-field spectroscopies on dimer systems. The results show that the TPL spectra can provide additional data on the electromagnetic modes of the nanostructures. In particular, multipolar-like resonances that cannot be observed in the scattering response are clearly resolved with TPL characterization.

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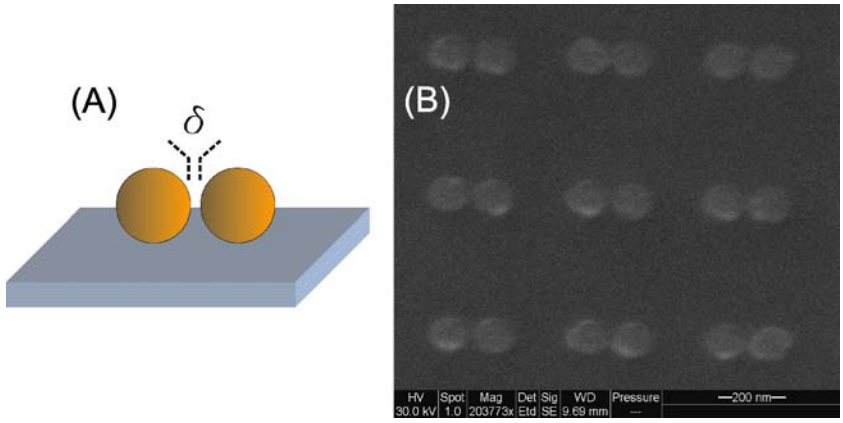

Figure 1. (A) Schematic of a single dimer. (B) SEM micrograph of part of an array of gold particle dimers.

Experimental results

The configuration under study consists of a periodic arrangement of gold dimers lying on top of indiumtin-oxide-coated glass substrate. The particles have roughly a cylindrical shape with diameter of about 100 *nm* and height of 15 *nm*. The pitch of the grating, fixed at 400 *nm* has been chosen to maximize the signal from the ensemble without interfering significantly with the near-field coupling between the particles of each single dimer [7]. Each sample prepared by a combination of conventional e-beam lithography and thin-film deposition is made of several 50 $\mu m \times 50\ \mu m$ matrices with different separation distances δ ranging from contact (0 *nm*−80 *nm*).

To test the quality of the fabricated dimers, we first measure their scattering spectroscopy as a function of the interparticle distance δ. For this purpose, we use a transmission optical microscope under dark-field illumination ($NA = 0.8 - 0.92$), connected to a microspectrometer via a multimode optical fiber. The evolution of the central resonance wavelength on δ is plotted in Figure 2 or both longitudinal and transverse polarizations.

In agreement with previous works, one can observe a red shift in the longitudinal polarization and a blue shift in the transverse one when decreasing δ [8]. This behavior can be explained using a simple dipolar model based on the interaction of polarization charges formed at the particles surface [1]. In the case of longitudinal polarization, the increasing compensation of surface charges when the particles get closer induces weaker repulsion forces corresponding to higher resonance wavelengths. On the contrary, for an incident field orthogonal to the dimer axis, these forces tend to increase giving rise to a slight blue shift.

To measure the TPL response of the dimers, the sample was placed upside-down in the sample plane of

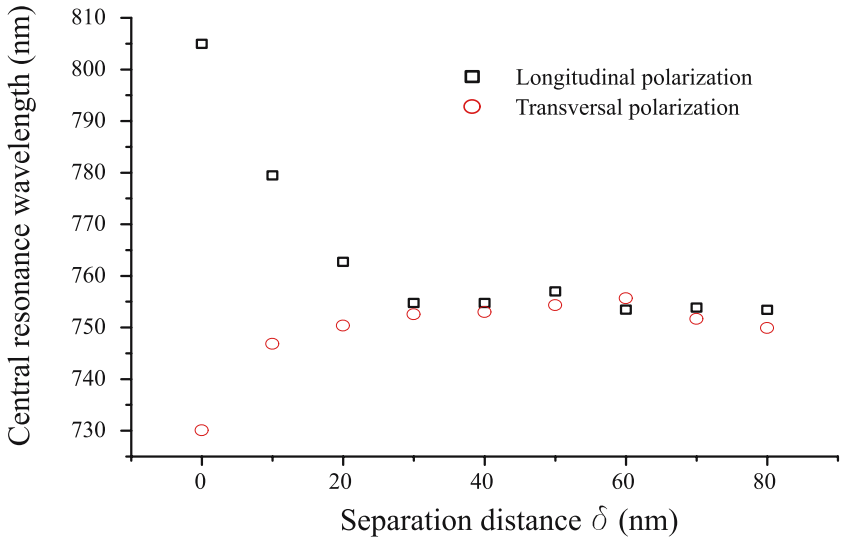

Figure 2. Evolution of the extinction resonance wavelength with the separation distance δ.

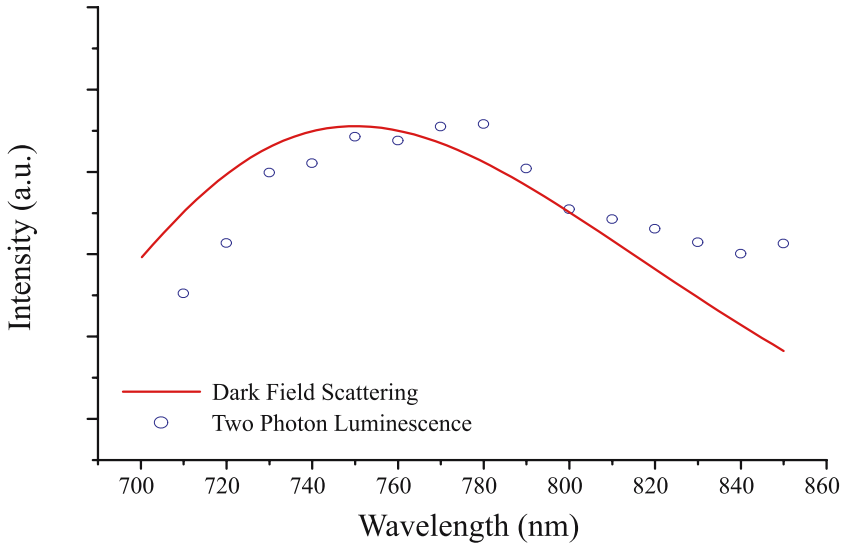

Figure 3. Comparison of TPL and far-field spectrum for $\delta = 30\ nm$ under longitudinal polarization.

an inverted laser scanning nonlinear microscope. The illumination was performed with a Kerr-lens mode-locked Ti/Sapphire laser, which delivers 150 *fs* pulses at a repetition rate of $f = 76\ MHz$. After attenuation with a tunable neutral density filter, the laser beam is sent to the sample surface through a microscope objective ($20\times$, $NA = 0.45$) and scanned over the matrices by using two galvanometric mirrors. To obtain the TPL spectral response of the dimers, the laser is stepwise tuned throughout the wavelength range ($700\ nm - 900\ nm$). Constant power at the sample plane is ensured by tuning the neutral density filter. For the measurements presented in this paper, the average power entering the microscope was 25 mW.

For each incident wavelength, the signal emitted by the dimers is collected by the same microscope objective and optically filtered through a BG39 filter. Finally, the TPL is detected using a photomultiplier tube (Hamamatsu, H9305-04) that is located at the output port of the microscope. It is recorded as a function of scanner position to form a TPL image. In post-processing, the average of the signal is calculated both inside and outside the dimer matrix for background subtraction. The difference is called TPL signal in the following.

Figure 3 shows the TPL spectrum under longitudinal polarization for dimers designed to have 30 *nm* separation distance. The TPL signal displays a clear

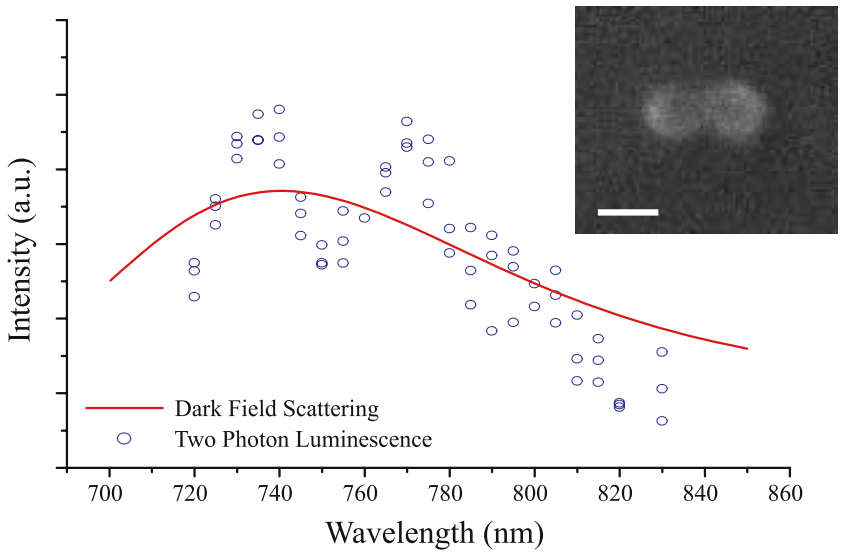

Figure 4. Comparison of TPL and far-field for touching dimers ($\delta = 0\ nm$) under longitudinal polarization. Inset: SEM micrograph of one of the dimers after TPL measurement (scale bar: 100 *nm*).

resonance, similar to the scattering one. For the same incident power, the TPL signal in transversal polarization is indistinguishable from the noise level, confirming that our measurement is mainly sensitive to the intense local field in the gap between the two particles.

For gap distances $\delta < 20\ nm$ where the highest local field enhancement is expected, the TPL measurements, performed with the same incident power, seem to engender a structural modification with resonances significantly blue-shifted compared to the initial scattering spectra. Additional TPL measurements after the entire wavelength scan indicate that the change occurred at the beginning of the measurement sequence. This was confirmed by a new set of scattering measurements that give similar new resonance wavelengths. Because the resonances are blue-shifted under longitudinal polarization, we can assume that the particles did not fuse. This is corroborated by scanning electron microscopic imaging that shows that after the TPL measurement, each particle is reduced in diameter to approximately $90\ nm$ and may thus get higher.

In the particular case of touching particles, a clear double peak resonance that does not appear in the scattering is observed (see Figure 4). This behavior is really similar to what is predicted by simulations from references [7] and [9], although it has never been reported experimentally. The shorter wavelength peak is attributed to a quadrupolar-like resonance resulting from retardation effects in the dimers that act as an effective bigger particle. The TPL information for such structures becomes of major importance, as it may help to better predict and/or understand the optical response of molecules located at their vicinity.

Conclusions

We have demonstrated that TPL can be used to assess the spectral near-field response of periodic ensembles of resonant gold dimers. Our measurements provide additional data to far-field spectroscopy that may be determinant for their application to enhanced spectroscopy and sensing. Further elaborations are in progress to avoid the structural modification of the nanostructures during their characterization.

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