Direct observation of localized surface plasmon coupling

J. R. Krenn, J. C. Weeber, A. Dereux, E. Bourillot, and J. P. Goudonnet
Optique Submicronique, Université de Bourgogne, Boîte Postale 47870, F-21078 Dijon Cedex, France

B. Schider, A. Leitner, and F. R. Aussenegg
Institut für Experimentalphysik, Universität Graz, Universitätsplatz 5, A-8010 Graz, Austria

C. Girard
CEMES, 29 rue Jeanne Marvig, BP 4347, F-31055 Toulouse Cedex 4, France
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We report on the direct observation of localized surface plasmon coupling using a photon scanning tunneling microscope. The surface plasmons are excited in gold nanostructures tailored by electron beam lithography. Electromagnetic energy transfer from a resonantly excited nanoparticle to a nanowire, which is not directly excited by the incident light is observed. Our experimental results appear to be in good agreement with theoretical computations based on Green's dyadic technique. [S0163-1829(99)08931-6]

I. INTRODUCTION

Nanoscale noble metal structures can exhibit anomalous optical extinction in the visible spectral range due to resonantly driven electron plasma oscillations (localized surface plasmons, LSP's).[1] The spectral position of the LSP resonance depends mainly on the structure geometry and the polarization state of the exciting light.[2] Due to its resonant character LSP excitation is accompanied with a strongly localized field enhancement around the nanostructures.[2] These properties make such structures interesting in the context of future nanooptical applications, i.e., guiding and controlling light on the submicrometer scale.

Although intensively investigated with far-field methods, little is still known about the optical near-fields around nanoscale metal structures. Such knowledge is highly desirable in order to tailor well-defined nanooptical devices, a task that is feasible today using advanced lithography techniques. Indeed, direct mapping of LSP near fields is accessible due to the development of near-field optical microscopy.[3] This technique has already been employed to study various metal geometries supporting LSP's. Experimental work focused on the local field enhancement and the spatial field distribution around nanoparticles[4,5] and nanoscale defects on metal thin films[6–10] were recently reported. Additionally, coupling effects of LSP fields were investigated. These effects are expected to occur for nanostructures in immediate vicinity of each other and can be described as dipole-dipole coupling[2,11] or in terms of *near-field* scattering.[12] A laterally squeezed optical near field due to LSP coupling was recently observed on an ensemble of linearly aligned gold nanoparticles[13]. Electromagnetic energy transport along a closely packed linear chain of nanoscale gold spheres following a local excitation was proposed in Ref. 14. Another example of LSP coupling was discussed for a local-field enhancement between a metal-probe tip and a metal sample in apertureless scanning near-field optical microscopy.[15] Despite these rather attractive properties there are to date, to the best of our knowledge, no spatially resolved experimental data demonstrating electromagnetic coupling between *two* well-defined isolated metal nanostructures. In this paper, we use a photon scanning tunneling microscope[16] (PSTM) to demonstrate an example of electromagnetic coupling between individual gold nanostructures. To evidence such a coupling, we use a resonant single particle as a local source to excite a nanowire placed in the close vicinity of the nanosource. The long axis of the nanowire is oriented such that it is not directly exicted by the incident field. Since the resonance frequency of the surface mode sustained by a metal particle depends strongly on its geometry, a proper choice of the incoming field's wavelength and polarization state allows such a selective excitation of the single particle.

II. EXPERIMENTAL AND THEORETICAL BACKGROUND

In our PSTM setup the sample is illuminated by an evanescent surface wave generated by total internal reflection through a glass prism of a TM-polarized laser beam (angle of incidence 60°). Two kinds of lasers were used in the following experiments, a red He-Ne with a wavelength of $\lambda = 633$ nm and a Titane:Sapphire tunable from $\lambda = 700$ to $\lambda = 820$ nm. The resulting optical near fields are probed by a tapered dielectric optical fiber produced by a standard heat-and-pull technique. The signal picked up by the fiber is converted with a photomultiplier. The fiber tip is approached to the sample with a piezo actuator until an exponential increase of the detected signal reveals the evanescent field and thus the immediate vicinity of the sample surface (within the decay length of the evanescent field in the order of 150 nm). The PSTM images provide maps of the spatial distribution of the optical near-field intensity, which are acquired by scanning the fiber tip in a *constant height* over the sample surface. Between two successive images the tip is approached a few nanometers closer to the sample surface until the tip touches the sample structure, thereby indicating the position of the structures. Before this final approach, no change in the tip morphology could occur. The PSTM images shown here

were acquired just prior to touching the sample with the tip, so that we can estimate to a few nanometers (≈ 10 nm) the actual distance between the fiber tip extremity and the surface of the sample structures. After touching the sample the fiber tip was replaced immediately. The whole PSTM system was implemented in an atomic force microscope (AFM, *Digital Instruments D3000*). Before and after the PSTM measurement, the fiber tip was replaced by an AFM tip to check the sample topography.

For the theoretical framework of our experiments we apply the Green's dyadic technique (GDT).[17–19] This method has proven to be a powerful approach for solving the full set of Maxwell's equations in the case of the interaction of light with nanoscale objects of arbitrary shapes. The GDT has been applied successfully in the simulation of experimental results of near-field optical experiments. For example, an excellent agreement of the calculated square modulus of the electric field with experimental data has been found for PSTM measurements on dielectric nanoparticles.[17,20,21] This result is particularly interesting as the presence of the fiber tip was not accounted for in the calculations. This indicates that the PSTM signal measured with a dielectric tip is proportional to the local-electric field intensity over the sample. A similar good agreement was found in the case of gold nanoparticles[13] when a reasonable assumption about the finite size of the probe tip was taken into account. In the present work, the GDT is used not only to compare the numerical results with experimental ones but also as a tool to design the gold nanostructure geometries for presetting the values of the LSP resonance wavelengths. The validity of our approach was verified by measuring the LSP resonance wavelengths of the produced nanostructures by far-field optical transmission spectroscopy. We found that the measured resonance wavelengths correspond to the predicted values within a maximum deviation of about 20 nm, which is well within the homogeneous spectral linewidth of the LSP peaks. We note that for a nanostructure whose diameter exceeds the Rayleigh limit[2] the spectral position of the optical transmission minimum does not necessarily coincide with the wavelength at which the LSP near-field intensity is maximum.[12] However, we have verified numerically that this is the case for the nanostructures studied in this paper.

III. RESULTS AND DISCUSSION

Our sample consists of gold particles (surface projection 120×60 nm^2, height 40 nm) and wire structures (surface projection 660×60 nm^2, height 40 nm) deposited on an indium-tin-oxide (ITO)-doped glass substrate. The sample topology resulting from a nanofabrication process based on electron-beam-lithography[22] was checked by the AFM image shown in Fig. 1. A nanoparticle and a nanowire, respectively, are positioned close to each other for coupling studies (structure *C* in Fig. 1), the single wire (structure *B* in Fig. 1) and the three individual particles (structure *A* in Fig. 1) located in the upper part of the image serve for reference. The sample geometry was calculated to allow resonant LSP excitation of the nanoparticles at a wavelength of 740 nm, when using a TM-polarized incident beam (i.e., polarized in the *yz* plane) in total internal reflection. For this illumination condition, no LSP mode of the nanowire is expected to be excited directly by the incident light. However, we expect that a LSP mode of the nanowire corresponding to electron plasma oscillations in the direction of the *x* axis can be excited by the highly inhomogeneous LSP field of the nanoparticle. To find an optimized coupling geometry between nanoparticle and wire we consider the spatial near-field distribution around the resonantly excited particle. Due to our illumination geometry we find the main contribution of the near-field intensity scattered by the nanoparticles to be in *forward* direction, with respect to the propagation direction of the evanescent surface wave generated by the total internal reflection illumination (i.e., along the *y* axis). Thus, by placing the nanowire in a distance of 30 nm from the particle at a position as seen in Fig. 1 (structure *C*), we expect from our numerical results an electromagnetic coupling between the two nanostructures. We mention that the redshift of the particle LSP resonance wavelength due to the presence of the wire[2] was calculated to be within the width of the resonance peak of the particle LSP and thus to be negligible for our experiment. Finally, we note that if the TM-polarized incident wavelength is 633 nm, the numerical computations indicate that no LSP excitation occurs for the single particles or the nanowires.

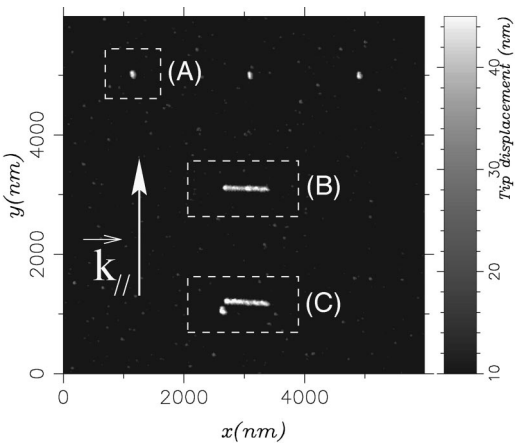

FIG. 1. Atomic force microscope image of the sample. All the structures are made of gold with a volume of $120\times 60\times 40$ nm^3 for the particles and $660\times 60\times 40$ nm^3 for the nanowires. The white arrow indicates the propagation direction of the incident surface wave obtained by total internal reflection.

The measured optical near-field distribution on the sample area imaged with the AFM in Fig. 1 is shown in Fig. 2 for an incident wavelength of 633 nm. It appears that the two wires exhibits a much stronger optical responses than the three isolated particles. Moreover, no signicant differences can be observed in the near-field intensity distribution detected above the isolated nanowire and the system consisting of the particle placed close to the nanowire [respectively labeled (*B*) and (*C*) on Fig. 1]. Such a result leads to the conclusion that for $\lambda = 633$ nm, no measurable coupling occurs between the nanowire and the particle of structure (*C*). As previously mentioned, for a incident a wavelength of 633 nm, neither the particles nor the wires LSP's can be resonantly excited. As a consequence, the near-field intensity distribution just mirrors the polarizability of each particle and thus, the volume of the individual structures. This is in agreement with the strong-optical response observed above the nanowires since the volume of the wires is more than five time larger

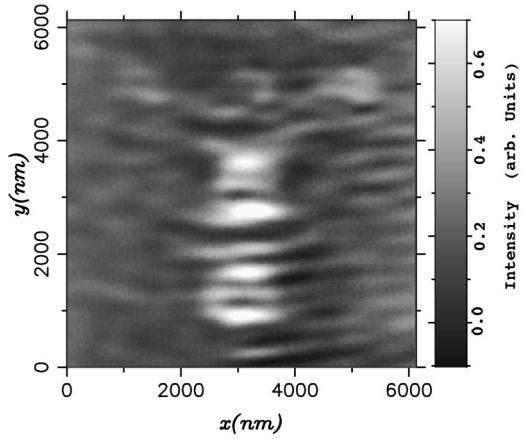

FIG. 2. PSTM image of the area shows on Fig. 1 for a TM-polarized incident He-Ne laser beam with a wavelength of 633 nm. The angle of incidence is fixed to 60°. For $\lambda = 633$ nm, the particles and the nanowires are not resonant.

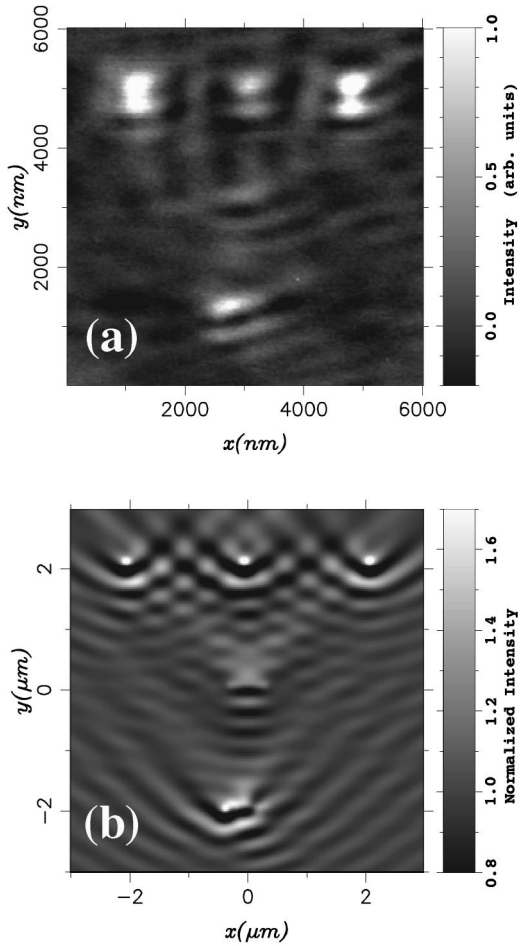

FIG. 3. (a) PSTM image of area shows on Fig. 1 for a TM-polarized incident Ti:Sapphire laser beam with a wavelength of 740 nm. The particles are resonantly excited by the incident light while the incident polarization prevents from a direct excitation of the long axis of the nanowires. (b) Theoretical electric near-field intensity map (normalized with respect to the incident one). The illumination conditions used for the calculation are similar to the experimental conditions.

than the one of each isolated particle.

The near-field optical image displayed in Fig. 3(a) has been obtained with an incident wavelength of $\lambda = 740$ nm. We observe a strong near-field intensity around the three resonantly excited single particles (*A*). The intensity enhancement of about two with respect to the incident intensity is in accordance with previously published data.[4] The spatial intensity distribution with *two* intensity maxima aligned in the propagation direction of the incoming surface wave correspond to the recently observed LSP intensity around 100-nm diameter gold particles.[13] Due to a slightly different shape, the intensity around the particle in the middle position is not so high when compared to the intensity around the other particles. As the resonance condition is not fulfilled for the isolated wire (structure *B* in Fig. 1), the near-field close to it is much less intense than close to the particles. The measured near-field intensity close to the nanoparticles as well as close to the nanowire are in good agreement with the calculated intensity of the electric field (normalized to the incident intensity), see Fig. 3(b). The calculation was performed for the actual total internal reflection illumination of the experiment. The numerical application of the GDT used a real–space discretization of the gold nanostructures into $20\times20\times20$-nm^3 cells. The effective dielectric function of the ITO substrate is 2.37, the one of gold was taken from Ref. 23. We found the best agreement of the calculation with the experimental data assuming the electric field intensity in a plane 140 nm over the substrate plane. As already found in Ref. 13 this height does not correspond to the actual distance from the fiber tip extremity to the sample surface when acquiring the PSTM image, which we know to be a few nanometers. Rather this value should be interpreted as an *effective* observation plane resulting from a signal detection integrated over the finite size of the fiber tip.

We now analyze the near-field intensity around the nanoparticle and wire close to each other (structure *C* in Fig. 1). Clearly the spatial intensity distribution is different from that for a single particle (structure *A* in Fig. 1). It rather resembles the optical near-field distribution around the isolated nanowire (structure *B* in Fig. 1), but with a maximum intensity value about 1.5 times higher. When comparing the measured optical near-field image to the calculated intensity map, we find a remarkable coincidence. The distinctive feature of the optical intensity distribution on area *C* is the inclination of the observed elongated intensity maxima. This inclination forms an angle of 15° with respect to the *x* axis, which is well reproduced by the calculation. We conclude that we observe electromagnetic energy transfer from the nanoparticle to the wire. In other words, the nanoparticle and the wire form a coupled system, which supports a LSP mode that can be excited by the given illumination conditions.

In order to change the geometrical coupling condition between the nanoparticle and the wire we continued to scan the sample with the fiber tip after acquiring the image shown in Fig. 3(a). We thus touched and moved the structures. An AFM image of the modified lateral distribution is shown in Fig. 4. Note that the curved shapes of the nanoparticles (*A*) and the nonhomogeneous shape of the nanocylinder in area (*D*) are artifacts related to the fact that the AFM tip moved the structures during scanning. Figure 5(a) shows the PSTM image that was recorded *before* the AFM check of Fig. 4. While the optical near-field intensities around the isolated

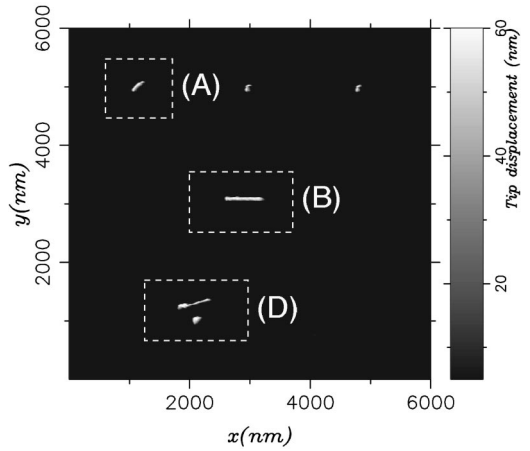

FIG. 4. Atomic force microscope image of the modified structure.

nanostructures (structures *A* and *B* in Fig. 4) remain unchanged, we now observe the intensity pattern typical for an isolated nanoparticle at the position of the particle and wire in close vicinity (structure *D* in Fig. 4). Again, the simulated image [Fig. 5(b)] shows a good agreement with the experimental data. We conclude that the nanoparticle in area (*D*) does not couple any more to the nanowire and thus responds to the exciting light wave like the isolated nanoparticles (*A*) in the upper part of the PSTM image.

IV. CONCLUSION

In summary, we have used a PSTM setup with a dielectric fiber tip to observe the coupling between the LSP field of a resonantly excited gold particle and a nanowire. The particle was excited by a TM-polarized incident surface wave propagating in the *y* direction, i.e., perpendicularly to the long axis of the nanowire (*x* axis). The illumination conditions prevent from a direct excitation of the long axis of the wire since the incident electric field has no component along the *x* direction. When the structure is excited at a proper wavelength, the particle acts as a nanosource of an evanescent field and transfers a part of its electromagnetic energy to the objects placed closed to it. As shown directly by imaging with the PSTM, the efficiency of the LSP-coupling mechanism depends critically on the position of the two nanostructures relative to each other. The good agreement we have found between experimental data and the numerical computations indicates that the Green's dyadic technique is reliable to describe near-field scattering by resonant metallic particles. Nevertheless, the deviation of the simulated intensity maps

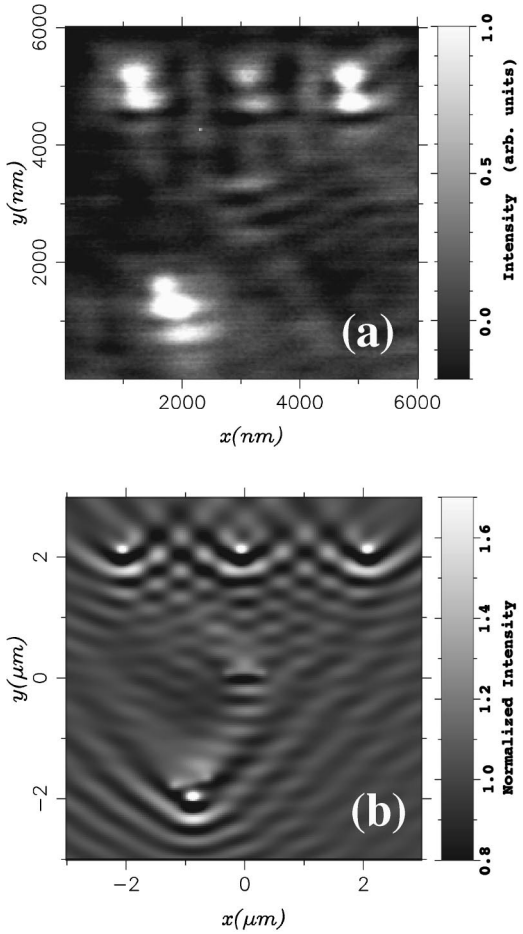

FIG. 5. (a) PSTM image detected above the area shows on Fig. 4. The illuminations conditions are similar to those of Fig. 3. (b) Theoretical electric near-field intensity computed above the modified structure.

from the experimental images lead us to further insight in the process of the near-field optical measurement. A deeper understanding of the near-field optical phenomena is necessary to investigate situations of technological interest. A combined use of several techniques as electron-beam lithography, numerical simulations and direct observation of near-field phenomena is an effective procedure to improve the understanding of near-field optical effects.

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