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Optical imaging with subnanometric vertical resolution using nanoparticle-based plasmonic probes

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ABSTRACT

We present images with subnanometric optical resolution using novel metal nanoparticle-based probes in a Field Enhancement Scanning Optical Microscope. The probe is built of silica microspheres decorated with silver nanoparticles, which act as enhancers of the optical field. The optical resolution is dependent on the wavelength and polarization of the exciting field, and the approach curves reveal the enhancement due to cavity modes between the plasmonic probe and the sample.

Metal nanoparticles (NPs) are today powerful tools having high impact in several areas of the nanosciences and biology. Among the many examples of applications of the NPs we can mention nano-biosensors [1], probes for high resolution optical microscopy [2], enhancers for detection of single molecules [3], hyperlocalization probes [4] and optical integrated circuits in the sub-wavelength scale [5]. Their wide range of applications is basically due to two related effects: localized plasmon resonances in the visible and a strong and confined enhancement of the electromagnetic near field. In this work we introduce a reliable and easy to build NP-based system, used as a probe of the Field Enhancement Scanning Optical Microscope (FESOM) [6]. Also, we show that with these probes, images of the HOPG surface with subnanometer vertical resolution can be recorded.

The spatial range of the field confinement is closely related to the size of the NPs, and, hence, with the expected resolution of the FESOM. One single NP attached to the end of a tip [2,7,8] would be the perfect probe, since it is the simplest and more predictable NP-based tip. However, it is extremely difficult to capture and keep one single and small NP on the apex of a macroscopic wire. We present here, an alternative approach to have a NP-based probe: NP-decorated silica microspheres. The spheres, having a very smooth surface, act as holders for the NPs and, also, as linkers between the nanoscopic NPs and the macroscopic wire. Silver NPs, with diameters of 5 nm on average, which are surface-modified with aminosilanes (*N*-[3-(trimethoxysilyl)propyl] diethylenetriamine) [9], were incubated for several hours at room temperature with 170 nm diameter SiO_2 microspheres covered with silanol surface groups (Bangs Laboratories, SS02N). Concentrations of both solutions were chosen for having about 3000 NPs per microsphere, in order to be close to the full coverage of the microsphere surface. Meanwhile we want the NPs to be almost in contact, we should preserve the granularity of the probe in order to have a confinement on the order of the particle size or less. The extinction spectrum of the colloidal solution is shown in Fig. 1a. The spectrum has a non-trivial structure, showing several peaks which reveal interaction between NPs [10]. Actually, non-interacting silver NPs have a single plasmon peak at about 420 nm, as shown in Fig. 1a. The very end of a mechanically cut silver wire was immersed for 10 min in the colloidal solution, and, as a result, a layer of the decorated spheres was adsorbed on the surface of the wire. Fig. 1 shows SEM pictures of the built structure. Fig. 1d suggests the NPs decorate efficiently and regularly the microspheres and those are attached to the wire. However, due to our SEM resolution, we can not appreciate in detail the distribution of the smaller NPs. We believe the NP coverage is close to percolation on the microsphere surface, based on the observation of the spectrum [10]. Also, tips prepared in the same way but using bare silica microspheres, do not establish a tunneling current, while the decorated ones easily do. Therefore, we conclude that there is a strong coupling between NPs, and, hence, the possibility to have strong enhancement around the structure. This assumption is corroborated by the approach curves as it will be shown below.

The experimental setup is fully described in Ref. [6] and shown schematically in Fig. 2. A HOPG-probe junction is illuminated from the side. The *z-piezo,* attached to the sample, is dithering about 0.1 nm at a frequency $\Omega = 5$ kHz. The optical signal at 2Ω [11–15], using a lock-in detection, is collected in backscattering. This higher harmonic demodulation technique improves the ratio between the near field signal and the interferometric background, due to the much higher nonlinearity of the near field as a function of the tip–sample distance.

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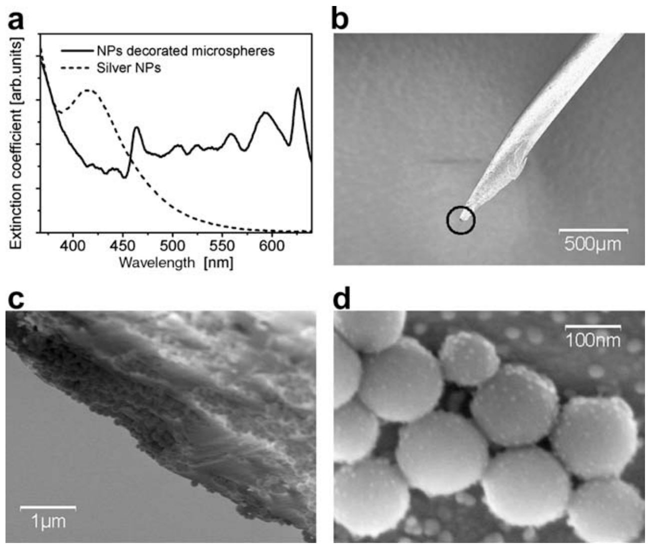

Fig. 1. The extinction spectrum of the colloidal solution of the NP-decorated microspheres is shown in (a). Multiple peaks in the spectrum reveal interaction between NPs. Non-interacting silver NPs spectrum is added for comparison. (b), (c) and (d) SEM images of the NP-based probes, with increasing resolution. Image (c) is the zoom of the circled zone in (b).

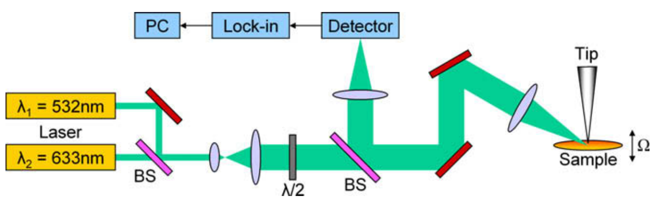

Fig. 2. Experimental setup scheme. The junction is illuminated from the side with a laser focused down to about 10 μm, which polarization can be controlled with a half waveplate. The sample is dithering at $\Omega = 5$ kHz. The scattered light is collected in backscattering with the same optics and detected with a PIN photodiode. The lock-in detection is performed at 2Ω.

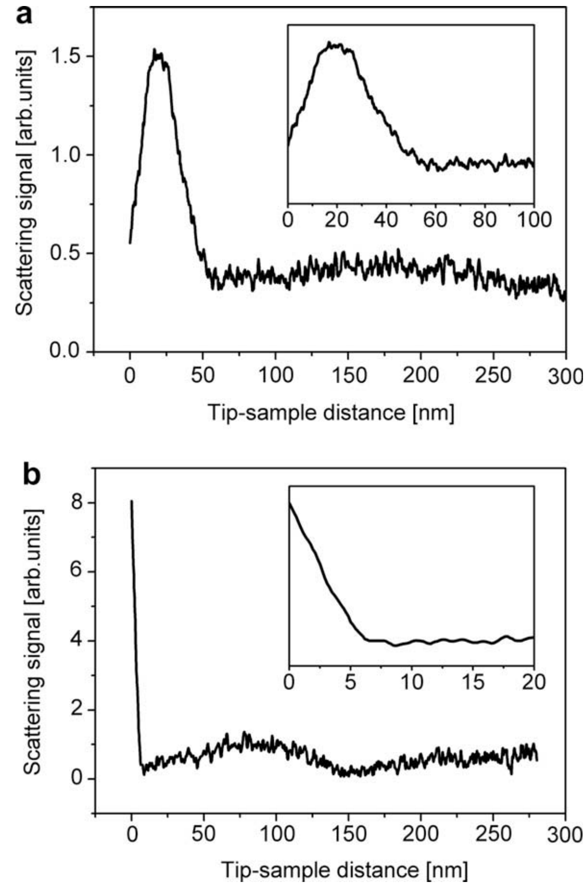

Fig. 3. Approach curves of the scattering signal at 2Ω. (a) 532 nm and (b) 633 nm incident wavelength (p-polarized). Curves have a clear dependence on the wavelength and show the signature of the field enhancement. The insets show enlarged scales for short distances.

Approach curves of the backscattered light as a function of the distance between the NP-based tip and the sample (HOPG) are recorded. The measurement of these curves is essential to characterize the enhancement of the field. In order to control the tip–sample distance, a ramp of voltage is applied to the z-piezo, with the feedback loop totally turned off. The sample approaches to the tip from a large distance (several wavelengths) until a given tunneling current is detected, followed by the retraction of the piezo. The tip–sample distance for which the preset tunneling current is reached, is defined as zero distance in the approach curves. We alternately illuminate the junction with a monomode CW doubled Nd:Yag laser (532 nm) or a He–Ne laser (633 nm), whose polarization can be controlled by half waveplates. Fig. 3 shows characteristic approach curves recorded with p-polarized light at both wavelengths. After a residual interferometric background collected at large distances, the signal suddenly goes up at very short tip–sample distances, as a signature of the field enhancement. These kind of features are already known since the early seminal work of Fischer and Pohl [16] on plasmonic probes. However, there are clear differences between both curves. For 532 nm illumination (a), there is an increment up to a distance of about 20 nm, where the signal starts to decrease. Conversely, for 633 nm illumination (b), the signal does not show up until a distance of about 6 nm, and then it grows monotonically, reaching higher values than in the case (a). We assign this effect to a plasmon red-shift due to cavity modes when the tip approaches the sample to very short distances [17], producing the reduction of the green signal and the appearing of the red one. Several authors reported red-shifts in various systems, for NP–NP [18], metallic tip–metallic sample [19] and a variety of composite configurations [20]. The spatial extent and the wavelength of the (a) curve suggest that the enhancement is provided by a collective mode of NPs instead of the mode of a single NP. Despite the unknown of the actual NP-configuration, the approach curves show that, tuning the laser to the red, nanometer vertical sensitivity should be obtained. We understand this behavior in terms of the high sensitivity of the wavelength-shift of the cavity modes for very short distances.

The approach curves are highly repetitive and stable over several days, until some degradation occurs, probably related either with the oxidation and degradation of the silver NPs in air or the oxidation of the wire supporting the probes. They are monitored frequently in order to register the progress on the behavior of the probe. Fig. 4 shows the evolution of those curves for a given probe as the time passes. Curves of Fig. 4a, taken during the first day, show an impressive stability, which also persists along the second day. Throughout the third day the curve changes to Fig. 4b(ii), although high resolution images still can be recorded. The forth day the degradation is accelerated, and during the same day the curve passes from Fig. 4b(iii) to (iv) and the resolution is totally lost. Different probes show approximately the same behavior, they can be used confidently over several days, which make these probes very attractive for imaging. The yield of the working tips, which show similar approach curves, is of about 1:5, with a statistics of about 50 trial tips.

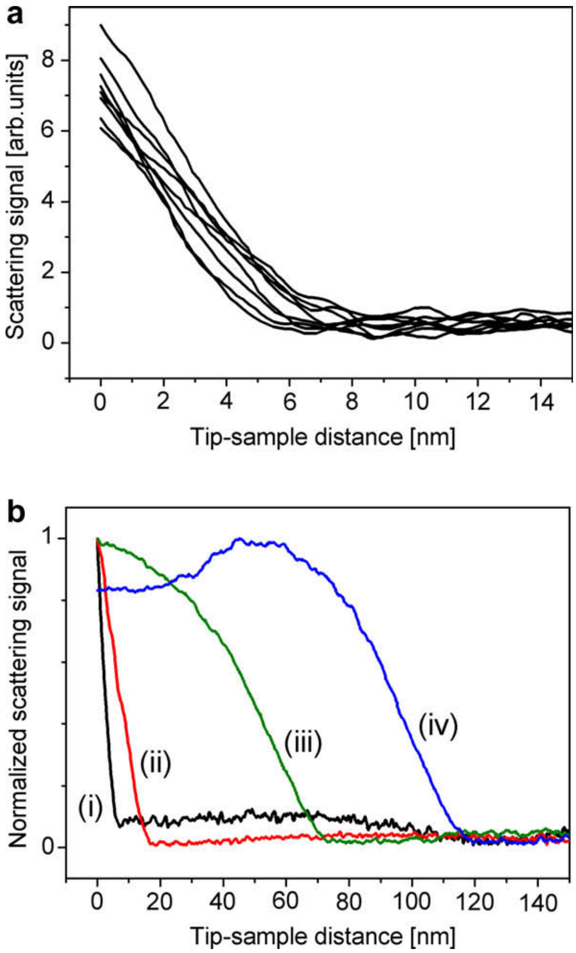

Fig. 4. Approach curves obtained on the first day are shown in (a). 633 nm incident light was used. The optical signal goes up at very short tip–sample distances. (b) Evolution of the approach curves during four days. From left to right: (i) first day, (ii) third day, (iii) and (iv) forth day.

Fig. 5a shows the optical image of a HOPG surface recorded at constant height (without feedback loops) around the zero distance point. High resolution images are only obtained for p-polarized 633 nm incident light. The resolution is totally lost either when the polarization is rotated 90° or the wavelength is tuned to the green. As it is well known, HOPG presents a very flat surface, with large atomically corrugated terraces separated by some mono – or few – layer steps. In order to compare the optical signals with the topographic corrugation, we record the topographic image (STM) immediately after obtaining the optical one. Two steps in the STM image are marked, one with an estimated height of 5 nm and the other one of less than 1nm in height. High optical resolution is clearly seen in both steps, indicating subnanometer sensitivity of the optical signal. Such a high vertical resolution can not be ascribed to any artifact since the signal values are fully out of range for any interferometric background (see Fig. 3). Also, the scattering intensity histogram of the FESOM image matches with the intensity of the enhancement peak in the approach curve, and it is much larger than the interferometric artifact. We finally would like to comment on the reversed contrast of the optical images, compared to the topographic ones. We are giving some arguments to try to explain this behavior, although we do not have a conclusive explanation. It was recently shown the optical response for NP dimers [21] as a function of the distance between the particles, for very short distances. In these systems, the maximum of the plasmon resonance shifts much faster as the dimer approaches to the contact point, and, moreover, in the touching regime, the plasmon resonances move on the reverse way and new resonances appear. This scenario is similar than the one in this work, where a NP probe is approaching the sample, and, therefore, some of the mentioned effects could appear in the last nanometer before the contact and in the tunneling regime. As the images are taken at a fixed wavelength, a depletion of the signal near the tunneling region, based on a rapid change of the resonance may cause the reverse contrast. As far as we can go, approach curves do not show a reversed behavior. However, so far, we do not have enough resolution and stability in the approach curves to see the signal behavior in the near tunneling regime, where the images have been recorded.

In conclusion, we built new plasmonic probes, based on nanoparticle decorated microspheres, which can be confidently used for imaging. Approach curves with the new probes, show clearly field enhancement at very short probe-sample distances, and cavity mode effects through their wavelength dependence. Being the finger-print of the expected performance of a probe, approach curves bring forward a very high optical resolution, since the optical signal shows monotonically fast changes over short distances. In effect, we found subnanometric vertical resolution in graphite images, when the probe is kept at a constant height while the sample is scanned. The expected lateral resolution is on the order of the vertical one. Also, a totally optical feedback loop is feasible, due to the sharp distance dependence of the approach curve.

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We wish to acknowledge Oscar Martínez for his continuous encouragement and helpful discussions. This work is supported by ANPCYT PICT 14209, CONICET PIP 5374 and Fundación Antorchas Grant No. 53900-9.

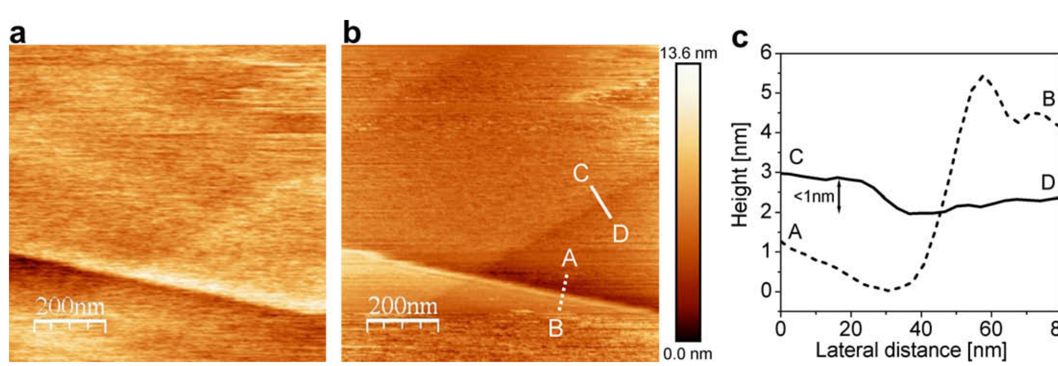

Fig. 5. (a) HOPG terraces recorded with the FESOM using NP-based probes and p-polarized 633 nm light. In (b) the STM topographic image is shown, with its color bar, for comparison and for the analysis of the heights. Lines marked in image (b) correspond to the profiles in (c). It can be seen that a subnanometer step is resolved in the optical image.

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