Enhanced Near-Field Imaging Contrasts of Silver Nanoparticles by Localized Surface Plasmon

Yun-Chorng Chang, Member, IEEE, Hsueh-Wei Chen, and Shih-Hui Chang, Member, IEEE

Abstract—Near-field images of Ag nanoparticles are studied using a near-field scanning optical microscopy (NSOM) operating at illumination mode with blue, green, and red probing lights. The obtained far-field intensity contrast between the nanoparticle and background strongly depends on the sizes of nanoparticles and the wavelength of probing light. Experimental NSOM images supported by theoretical 3-D finite-difference time-domain simulation demonstrate that the intensity contrast is enhanced at wavelength close to the localized surface plasmon resonance (LSPR) peak of the nanoparticle. The abilities to distinguish nanoparticles with different LSPR properties on the same substrate can lead to a material-specific NSOM imaging technique.

Index Terms—Near fields, plasmons.

I. INTRODUCTION

Techniques of nanoparticle detection have improved significantly for the demands of unprecedented high resolution in nanotechnologies. Information about the spatial distribution and chemical identity of nanoparticles provide vital information for both nano- and biosciences. Among different mapping techniques, optical methods offer fast, noninvasive, and highly sensitive detections for wide variety of materials. Various near-field imaging techniques have been developed to overcome the Abbe’s diffraction limit and achieve subwavelength spatial resolution [1]–[4]. In a recent report, material-specific particle recognition was achieved with sub-10 nm resolution due to the strong tip–substrate coupling in scattering-type near-field scanning optical microscopy (NSOM) [5].

The detection sensitivities can be further enhanced by the effects of localized surface plasmon resonance (LSPR) from metallic nanoparticles. The collective resonant oscillation of the conduction electrons of metallic nanoparticles is the origin of localized surface plasmon. The LSPR frequencies depend strongly on the shapes and sizes of the nanoparticles as well as the dielectric environments [6]. The LSPR spectrum of a single gold nanoparticle has been studied with the help of an aperture-type NSOM [7]. Similar results have also been reported using a scattering-type NSOM [8]. These reports indicated the potential of LSPR-assisted metallic nanoparticle imaging using NSOM technologies. However, the size dependence of the metallic nanoparticles and their corresponding NSOM images were not well reported. In this study, near-field images of Ag nanoparticles with different sizes are studied using experimental NSOM measurements and 3-D finite-difference time-domain (FDTD) simulation. It is found that the transmitted intensity from the NSOM probe and the image contrast are greatly affected by the LSPR of the nanoparticle. The intensity contrast becomes highest when the wavelength of the incident light matches the LSPR of the nanoparticle. The enhancement factor is proportional to the resonant quality factor. This property can be useful to identify or group different size, shape, and composites of particles on the same substrate.

II. EXPERIMENTS

Fabrications of Ag nanoparticle arrays were achieved by annealing 5 and 10 nm Ag thin films at 600 °C for 30 min inside a nitrogen-flowing oven. Double-side polished quartz substrates or silicon substrates were used for different subsequent analyses. Ag nanoparticles fabricated on top of silicon substrates were analyzed by a scanning electron microscopy (SEM). Fig. 1(a) and (b) was SEM images of the Ag nanoparticles fabricated from 5 and 10 nm of Ag thin film on top of silicon substrates, respectively. The size distributions of Ag nanoparticles were subsequently analyzed from the SEM images and the results were shown in Fig. 1(c). The size and its variation are larger...
for Ag nanoparticles fabricated from thicker films. A commercial ultraviolet-visible spectroscopy (UV-VIS) absorption spectrophotometer (Hitachi U-3010) was used to determine the surface plasmon resonance of the Ag nanoparticles, as shown in Fig. 1(d). Samples for the absorption measurements were grown on top of transparent quartz substrates. The absorption spectrum from the Ag nanoparticles fabricated from 5 nm film, curve (1), exhibits an absorption peak centered at 440 nm. This peak is referred as the scattering peak from the Ag nanoparticles. Curve (2) is the absorption spectrum measured from Ag nanoparticles fabricated from 10 nm films and two peaks centered at 420 and 630 nm are corresponding to the absorption and scattering peaks, respectively. The blue, green, and red arrows shown in Fig. 1(d) indicate the lasers used in the subsequent near-field measurements. The value below each arrow is its corresponding wavelength.

A commercial near-field scanning optical microscope scanner (Veeco Aurora-3) was used to obtain the near-field images of the Ag nanoparticles. The probe tip was a tapered single-mode fiber with an 80 nm aperture coated with 100 nm aluminum. Emission from a He–Ne laser ($\lambda = 633 \text{ nm}$) or frequency-doubled solid-state lasers ($\lambda = 475 \text{ nm}$ or $532 \text{ nm}$) was coupled into the spot in the NSOM image. For small Ag nanoparticles, fabricated from 5-nm-thin films, the surface plasmon resonance shifts close to the blocking by the Ag nanoparticle, which results in a dark particle and the background was discussed. Four nanoparticles are observed inside a highlighted polygon area in Fig. 2(a) and one particle is clearly larger than the other three. These three smaller nanoparticles exhibited a higher transmitted intensity contrast when using 633 nm laser, as shown in Fig. 2(b). The transmitted intensity contrast became smaller when using 532 nm laser and became the smallest when using 475 nm laser. The decrease in intensity contrast with decreasing excitation wavelength matched the trend shown in the spectrum range between 475 and 633 nm of curve (2) in Fig. 1(d). The intensity contrast was the highest when the excitation wavelength was close to the surface plasmon resonance of the Ag nanoparticles. Similar NSOM images of Ag nanoparticles fabricated from 5-nm-thin film are shown in Fig. 3. A rectangular area is also highlighted and three nanoparticles are observed inside this area. The size of the middle nanoparticle is smaller than the other two. NSOM images with different lasers are shown in Fig. 3(b), (c), and (d). These two nanoparticles on the side exhibited the highest intensity contrast when using 475 nm laser. The contrast became smaller with the increasing excitation laser wavelength. The decrease in intensity contrast with the increasing excitation wavelength matched the trend shown in curve (1) in Fig. 1(d).

From the results shown in Figs. 2 and 3, the intensity contrast for the same Ag nanoparticle depends strongly on the excitation wavelength. The contrast becomes higher when the excitation wavelength is closer to the surface plasmon resonance. For larger Ag nanoparticles, fabricated from 10-nm-thin films, the surface plasmon resonance wavelength is close to 630 nm. The strong light scattering of the red laser light ($\lambda = 633 \text{ nm}$) by the Ag nanoparticle results in a higher transmitted light intensity from the Ag nanoparticle as shown in Fig. 2(b). The transmitted intensity contrast became smaller when using 633 nm laser, as shown in Fig. 2(b). The transmitted intensity contrast became smaller when using 532 nm laser and became the smallest when using 475 nm laser. The decrease in intensity contrast with decreasing excitation wavelength matched the trend shown in the spectrum range between 475 and 633 nm of curve (2) in Fig. 1(d). The intensity contrast was the highest when the excitation wavelength was close to the surface plasmon resonance of the Ag nanoparticles. Similar NSOM images of Ag nanoparticles fabricated from 5-nm-thin film are shown in Fig. 3. A rectangular area is also highlighted and three nanoparticles are observed inside this area. The size of the middle nanoparticle is smaller than the other two. NSOM images with different lasers are shown in Fig. 3(b), (c), and (d). These two nanoparticles on the side exhibited the highest intensity contrast when using 475 nm laser. The contrast became smaller with the increasing excitation laser wavelength. The decrease in intensity contrast with the increasing excitation wavelength matched the trend shown in curve (1) in Fig. 1(d).

NSOM images of Ag nanoparticles fabricated from 10-nm-thin films are shown in Fig. 2. The topography image of the sample is shown in Fig. 2(a), and the NSOM images using 633, 532, and 475 nm laser light are shown in Fig. 2(b), (c), and (d), respectively. It should be noted that these lasers were with different emission intensities, and comparisons of the absolute transmitted intensities between different lasers were irrelevant. Only the intensity contrast between the signal from the nanoparticle and the background was discussed. Four nanoparticles are observed inside a highlighted polygon area in Fig. 2(a) and one nanoparticle is clearly larger than the other three. These three smaller nanoparticles exhibited a higher transmitted intensity contrast when using 633 nm laser, as shown in Fig. 2(b). The transmitted intensity contrast became smaller when using 532 nm laser and became the smallest when using 475 nm laser. The decrease in intensity contrast with decreasing excitation wavelength matched the trend shown in the spectrum range between 475 and 633 nm of curve (2) in Fig. 1(d). The intensity contrast was the highest when the excitation wavelength was close to the surface plasmon resonance of the Ag nanoparticles. Similar NSOM images of Ag nanoparticles fabricated from 5-nm-thin film are shown in Fig. 3. A rectangular area is also highlighted and three nanoparticles are observed inside this area. The size of the middle nanoparticle is smaller than the other two. NSOM images with different lasers are shown in Fig. 3(b), (c), and (d). These two nanoparticles on the side exhibited the highest intensity contrast when using 475 nm laser. The contrast became smaller with the increasing excitation laser wavelength. The decrease in intensity contrast with the increasing excitation wavelength matched the trend shown in curve (1) in Fig. 1(d).

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image of a Ag nanoparticle is a bright spot when the laser wavelength matches its surface plasmon resonance. To illustrate contrast-enhanced NSOM image of a Ag nanoparticle due to LSPR, a full 3-D FDTD simulation was carried out. A Drude–Lorentzian model for the dielectric constant of silver is given as

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\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 - j\omega\gamma_p} + \sum_{p=1}^{2} \frac{\Delta\varepsilon_p\omega_p^2}{\omega^2 + 2j\omega\gamma_p - \omega_0^2}
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where \(\omega_p\) is the plasma frequency of the metal and \(\omega_p\) \(p = 1, 2\) are the Lorentz resonant frequencies, and \(\gamma\)'s are the damping constants. These parameters were obtained by fitting with the empirical dielectric constant of bulk Ag at wavelengths from 300 to 800 nm [9]. The Ag nanoparticle was modeled as a hemisphere shape due to the thermal annealing process in the experiments. The extinction spectrum of a Ag nanoparticle with diameter of 160 nm on a glass substrate was calculated and was shown as the curve (3) in Fig. 1(d). It resembles the absorption spectrum measured in the experiments. To obtain the near-field scanning image of the Ag nanoparticle, an NSOM tip operated at illumination mode was included in the FDTD grid that was similar to an earlier report [10]. The geometry of the region near the Ag nanoparticle is illustrated in Fig. 4(a). By positioning the tip at different locations around the Ag nanoparticle, the integrated far-field energy flux was collected as the intensity for each pixel [11]. Three different light sources with wavelengths at 632, 532, and 480 nm were used for 2-D scan over an area of 0.6 \(\mu\)m \(\times\) 0.6 \(\mu\)m around the Ag nanoparticle. The calculated scanning NSOM images at wavelengths 632, 532, 480 nm were shown in Fig. 4(b), (c), and (d), respectively. The color scale was normalized by the background signal when no particle was presented and all three color bars ranged from 0.5 to 2.7. The colors of red, green, and blue were assigned as the background color with color bar value equal to 1. The FDTD results demonstrate a consistent trend that the NSOM image of the Ag nanoparticle became brighter as the probing wavelength moved toward the LSPR peak. These results are consistent with our experimental observation, which indicate that on-resonant metal nanoparticles will enhance the light extraction from the NSOM tip by a factor of at least several times. Depending on the probing light wavelength relative to the LSPR peak of the nanoparticle, the scanning images show drastically difference in contrast. This property is useful for distinguishing nanoparticles of different sizes and is potential for differentiating nanoparticles of various materials.

IV. CONCLUSION

Ag nanoparticles fabricated by thermal annealing of Ag thin films were studied using an NSOM. The transmitted intensity by an NSOM operating at illumination mode was recorded when using light sources with different wavelengths. The transmitted intensity contrast between the Ag nanoparticle and the background is higher when the LSPR of the Ag nanoparticle matches the wavelength of the light source. This phenomenon is theoretically confirmed by the 3-D FDTD simulations. Therefore, Ag nanoparticles with controlled sizes can be distinguished by the NSOM in this study, while conventional atomic force microscopy (AFM) can only recognize the existence of nanoparticles. By modifying the surface of metal nanoparticles differently according to their sizes, one can obtain a material-specific NSOM images and reveal more material information compared to the current AFM images. Further development of this technique will be beneficial for future nanoimaging of biomolecular studies.

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REFERENCES

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