The phase-response effect of size-dependent optical enhancement in a single nanoparticle
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Optics Express Vol. 16, No. 13 9580-9586 JUN 23(2008)

With the rapid advance of nanophotonics, the optical effects of metal nanoparticles, such as surface plasmonic resonance (SPR), surface enhanced Raman scattering (SERS), are always attractive for basic physics and a lot of applications. Here, we tried to analyze near-field phase-response in a single silver nanoparticle (NP), a pair of NP, and extending to nanostructure. It is well-known that optical properties of metal nanoparticles strongly depend on plasmon resonance modes, which can be tuned via controlling the particle's size, shape and distance between each other [1]. The absorption/scattering cross-section of a particle expands significantly, contributing to the local electromagnetic (EM) field enhancement [2]. The effect of optical enhancement of nanoparticles has been studied in various experiments of surface-enhanced spectroscopy for a long time [3]. When the wavelength of incident light coincides with the wavelength of plasmon resonance, the absorption/scattering cross-section of a particle expands significantly [4]. The re-radiated electromagnetic (EM) field from the particle exhibits phase difference ($\phi$) relative to the incident EM field [5]. In this report, the plasmon-photon interaction is directly observed in the vicinity of silver nanoparticles through a near-field scanning optical microscope (NSOM). Our results manifest the correlation of phase-response and size-depend optical enhancement. Detailed interference behaviors between optical excitation and plasmon mediated re-radiation are revealed on a single particle basis. This observation facilitates nano-applications in controlling the spatial distribution of surface plasmon (SP) modes by means of nanostructures.

Such observation of SP phase response has been recently demonstrated in NSOM experiments on a single particle basis [6], but the SP phase dependency on particle size has not been well addressed. Through the study of size-/wavelength-dependent optical enhancement, we retrieved the phase shift of plasmonic re-radiation from the EM field distribution for each nanoparticle.
Figure 1(a) shows the scheme of experimental setup. Three lasers (a He-Ne laser ($\lambda=633$ nm) and two solid-state lasers ($\lambda=532$ nm, 488 nm) were used. They were individually coupled into the probe as the light source for exciting Ag nanoparticles. A random distribution of Ag nanoparticles with different sizes was fabricated by a high-temperature annealing technique. The diameter ranges from 15 nm to 150 nm. Fig. 1(b) gives the far-field absorption spectrum of Ag nanoparticle film measured by a UV/VIS/NIR spectrometer.

Figure 2 shows the simulation results. The purpose of this theoretical simulation is to qualitatively analyze the far-field interference between the re-radiated field from the nanoparticles and the propagating field from the fiber tip. We follow the instruction by Choi et al [6].

Fig. 3 displays NSOM images of a single silver nanoparticle of 50-nm diameter. For this particle, the plasmon resonance wavelength is about 530 nm and thus significantly larger resonance enhancement is...
provided by the 532-nm excitation. With the 633-nm excitation, though not at resonance, constructive interference exhibits between excitation and re-radiation, resulting in a weak, but positive signal. At 532 nm, which is on resonance, the particle dipolar re-radiation dominates, producing a stronger signal. But for the 488-nm excitation, the phase-shift of the polarizability resulted in a destructive interference, and thus a dip is observed. These results agree well with the simulations.

Fig. 3. Measured NSOM images of a 50-nm nanoparticle.

Fig. 4 outlines the particle size spectra of interfered optical far-field intensity with RGB excitations. The plasmon resonance peak of 633-nm excitation is located at the diameter of 75 nm, while that of 532-nm excitation is at 50 nm. The resonance peak of 488-nm excitation approaches its maximum toward a diameter of smaller than 40 nm. Ag nanoparticles with diameters larger than 75 nm can be employed to modulate the phase between \( \pi/2 \) and \( \pi \). Those are smaller than 75 nm can be used to control the phase between 0 and \( \pi \). Similarly, for the 532-nm excitation, the phase-modulation of \( \pi/2 \) is expected with 50-nm nanoparticles. These results validate the possibility of spatial manipulation of SP phases by modulating the size of metal nanoparticle or by selecting appropriate wavelengths.
In conclusion, our result manifests the correlation between plasmon resonance and the size of a single metal nanoparticle with the aid of a multiple-wavelength NSOM. We have shown that the size-/wavelength-dependent optical enhancement within a single silver nanoparticle can be revealed through isolated excitation. By visualizing the interference pattern between the plasmonic re-radiation and the excitation wave in the far field, the relative SP phase-shift across the resonant wavelength can be quantitatively extracted. The phase-response properties may be employed in allocating the spatial distribution of localized SP modes on a nanostructured surface.

REFERENCES: