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Photoemission Electron Microscopy for Analysis of Plasmonic Responses of Silver Nanoparticles

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Metallic nanoparticles have attracted considerable attention over the last decade due to their plasmonic properties. They exhibit localized surface plasmon resonances (LSPR) at particular excitation frequencies depending on the size, shape and material. The synthesis and properties of these particles have been extensively studied [1-3] and there are a wide variety of applications in medical tagging, sensing, and optical coupling [4-6]. As we move toward more complex devices it becomes critically important to understand and measure resonance coupling interactions of small groups of individual particles. The LSPR of a particular particle can be modified by proximity to a substrate or neighboring particles [7-13] and there is a need for characterization tools to analyze these dependencies for small systems.

Photoemission electron microscopy (PEEM) is a surface microscopy technique where a sample is illuminated with a high intensity photon source and the resulting photoemitted electrons are collected to form an image. In many cases the spatial distribution of light intensity in and around a sample can then be derived from an electron image [14]. This approach can also be extended to the characterization of plasmonic responses and has been used to observe propagating [15] as well as localized surface plasmons in various antenna structures[16]. In materials such as silver and gold a multi-photon process is required to produce a photo-emitted electron. This non-linear process produces strong contrast between areas of differing optical field strength. With its excellent spatial resolution and non-linear response PEEM is a promising tool for a detailed analysis of optical responses of metallic nanoparticles.

Nanoparticle systems were created by depositing citrate-capped silver nanospheres with a ~40nm diameter on to ITO coated borosilicate glass. The manufacturer's specifications indicate a LSPR peak at 422nm with a full width half max of ~40nm. A Spectra-Physics Ti:sapphire pulse laser tunable in the wavelength range from 780-900nm with 60fs pulse duration and a repetition rate of 100MHz is used as a photon source in combination with a Del Mar second harmonic generator and a wave plate for polarization control. Images are taken in 5nm steps in the wavelength interval $390\text{nm} < \lambda < 450\text{nm}$ with a resolution of ~60nm as illustrated in Fig. 1. The photoemission rate is calculated from the images and is compared to the predictions of an optical model evaluated in a finite-element method approach as shown in Fig. 2.

The experimental results compare favorable to the calculation. The closely spaced spheres produce a resonance peak at ~420nm in both experiment and simulation indicating that this LSPR is due to a coupling between the spheres. By exploring polarization and wavelength dependencies, geometric effects can be separated from substrate, particle size and material effects, and detailed understanding of optical coupling between the various sample portions can be obtained. We find that PEEM shows promise as a powerful characterization tool for these sub-wavelength optical systems.

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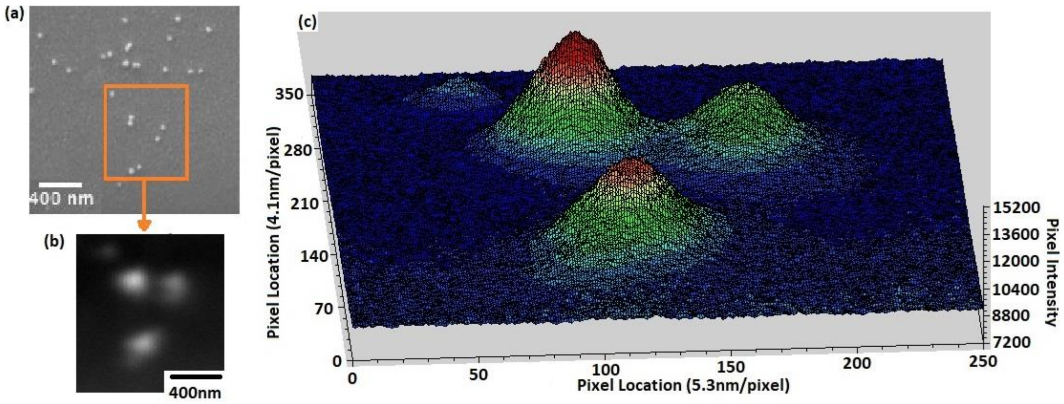

Fig 1. (a) SEM image of the silver sphere deposition on ITO. (b) PEEM micrograph taken at 420nm illumination. Note there are three grouping of two spheres with varied spacing and a single sphere in the upper left. (c) Plot of pixel intensity vs position for the PEEM image.

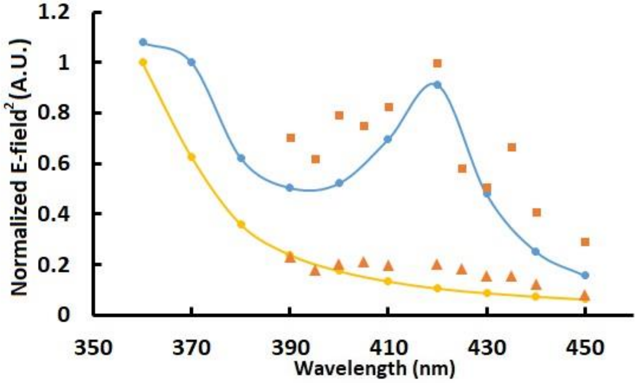

Fig 2. Blue curve: Spectrum of the normalized light intensity at the surface obtained from numerical calculations for two 40nm silver spheres with 2 nm separation. Yellow curve: single isolated sphere. The un-connected data points are experimental results from PEEM. Squares for very closely spaced spheres, triangles for single isolated sphere.