Plasmonic and Diffractive Coupling in 2D Arrays of Nanoparticles Produced by Electron Beam Lithography

Erin McLellan\textsuperscript{1}, Linda Gunnarsson\textsuperscript{2}, Tomas Rindzevicius\textsuperscript{2}, Mikael Kall\textsuperscript{2}, Shengli Zou\textsuperscript{3}, Kenneth Spears\textsuperscript{3}, George Schatz\textsuperscript{3}, and Richard Van Duyne\textsuperscript{3}
\textsuperscript{1}Chemistry, Northwestern University, 2145 Sheridan Rd, Evanston, IL, 60208-3113
\textsuperscript{2}Applied Physics, Chalmers University of Technology, Gothenburg, SE412-96, Sweden
\textsuperscript{3}Chemistry, Northwestern University, Evanston, IL, 60208-3113

ABSTRACT

Nanofabrication is one of the driving forces leading to developments in a variety of fields including microelectronics, medicine, and sensors. Precise control over nanoscale architecture is an essential aspect in relating new size-dependent material properties. Both direct write methods and natural lithography's offer a unique opportunity to fabricate “user-defined” writing of nanostructures in a wide range of materials. Electron Beam Lithography (EBL) and Nanosphere Lithography (NSL) provide the opportunity to fabricate precise nanostructures on a wide variety of substrates with a large range of materials. Using electrodynamics calculations, Schatz and coworkers have discovered one and two dimensional array structures that produce remarkably narrow plasmon resonance spectra upon irradiation with light that is polarized perpendicularly to the array axis. In order to investigate these interactions, precise control of nanoparticle orientation, size, shape and spacing is necessary. If the overall structures have excessive defects then the effect may not be seen. For the two dimensional arrays, to have the best control over array fabrication and to look at these interactions experimentally, EBL was used to construct both hexagonal arrays of circular cylinders and the Kagome lattice. The interparticle spacing in each of these structures was varied systematically. Dark field microscopy was used to look at overall sample homogeneity and collect the single particle plasmon resonance spectrum. Additionally, both dark-field and extinction spectroscopies were used to look at the bulk spectral properties of each array type and each spacing. In investigating of the two dimensional arrays, the Kagome structure was also compared to samples produced by traditional NSL to study the optical interaction of defects, domains, and overall sample uniformity on the shape and location of the plasmon resonance. This work illustrates a deeper understanding in the nature of the optical coupling in nanostructures and this knowledge can be utilized in the future to fabricate designer (tailor made) substrates for plasmonic and surface-enhanced raman applications.
INTRODUCTION

Assemblies of nanoparticles often can be used to provide special functionalities that are important in sensing [1], optical waveguides [2], and filters [3]. The use of assemblies, rather than single particles, offers the ability to average a signal across several similar particles (increasing intensity and eliminating discrepancies caused by defects) and the miniaturizing equipment is much simpler. Since the design of a practical plasmonic nanodevice relies heavily on arrays of noble metal nanoparticles, the interactions between these nanoparticles is a crucial and often overlooked design parameter. These interactions can be either short or long range for a variety of structure types including both highly dense array structures [4, 5] and individual pairs of nanoparticles [6]. They can be measured and studied by observing changes in the LSPR peak shape and position. Theoretical calculations also show these unique interactions. For example, previous work by Schatz et al. has predicted narrowed plasmon peaks in two-dimensional [7] and one-dimensional arrays [8, 9, 10] as a result of diffractive interactions between the particles. Van Duyne et al. also proved experimentally this diffractive coupling phenomena for the one-dimensional chains. [11] For these chains of particles above a critical size and with polarization and wave vectors taken to be perpendicular to the array axis, narrow peaks with widths less than 1 nm were reported. The narrow peaks are caused by the coherent interactions between the particles when the incident wavelength is close to the interparticle distance. [8, 10] Similar criteria hold true for the two-dimensional arrays, with a less dramatic effect in the narrowing of the plasmon, but still useful for creating better devices. By taking advantage of these coherent interactions, it is possible to create nanodevices with narrow lines that could lead to better sensing capabilities than are possible with isolated metal particles or aggregates of particles.

Methods for preparing nanoparticle arrays vary as widely as their uses. Standard lithographic techniques can be broken into two major categories, direct-write methods and natural lithographies. Natural lithographies, including nanosphere lithography [12, 13], are massively parallel and offer an inexpensive and rapid method for fabricating a large array of nanostructured materials. They, however, are limited by restricted lattice/inter-particle spacings, shapes, and sizes that can be produced, as well as a large range of defects that occur in the structure. On the other hand, direct write methods, such as photolithography [14], dip-pen lithography [15], and electron beam lithography (EBL) [16], offer fine control of size, shape, and lattice spacing, as well as few defects. Of the major problems associated with direct write methods are the serial nature of the process and the higher cost associated with production of arrays. EBL was chosen for this project because fine control over sample morphology was crucial.

Figure 1. (A) SEM image of NSL-like arrays with an interparticle spacing of 190 nm and (B) SEM image of 2D hexagonal array of cylinders with an interparticle spacing of 300 nm. Particle heights for both systems was 30 nm.
(based on theoretical modeling) to whether or not the sharp plasmon was going to be observed.

**EXPERIMENTAL DETAILS**

**Materials**
Ag (99.99%) and Ti purchased from Kurt J. Lesker (Evanston, IL). Glass substrates were 25mm by 25mm, no. 2 cover slips from Fisher Scientific (Pittsburgh, PA). Pretreatment of the glass substrates required H₂SO₄, H₂O₂, and NH₄OH, and the resist developer, hexylacetate were all obtained from Aldrich Chemicals. The resist, ZEP 520 was purchased from Nippon ZEON Ltd. Shipley Remover 1165 was purchased from Microchem Inc.

**Array Fabrication**
The samples were prepared by EBL on cleaned number 2 cover glass slips. After cleaning the glass was spin-coated (6000 rpm, 1 min) with a 60 nm thin film of an electron-sensitive resist, ZEP 520 diluted 1:2 in aniline. Before the pattern was exposed, the resist film was coated resistively with a 10 nm thin film of gold to make the surface conductive. The resolution of the EBL system used (JEOL 9300FS) is approximately 20 nm, employing an accelerating voltage of 1000 kV. After exposure, the Au film was removed by etching in an aqueous. The patterns were then developed in hexylacetate, creating a patterned resist film on top of which silver was deposited in a high-vacuum thin film vapor deposition system (AVAC HVC 600). The resist was dissolved in a strong solvent (Shipley Remover 1165), which also removes the metal deposited on the top of the resist. To ensure that the metal film on top of the resist does not have any physical contact with the metal deposited directly on the substrate (Figure 1A and 1B).

**Optical Measurements**
All optical measurements were made using an inverted microscope (Eclipse TE300, Nikon Instruments) and a fiber coupled to a miniature grating spectrometer (AvaSpec 2048, Avantes). The scattering measurements reported here were recorded over the range 350-850 nm. White light from the TE300 lamp was collimated before being passed through the sample. The scattered light was collected with both 60x and 10x objectives. A color video camera was also attached to the front port to collect optical images of the particle lines. A dark-field condenser was used to collect the light scattered by the nanoparticle lines.

**Scanning Electron Microscopy (SEM)**
SEM images were obtained using a Phillips FEI SEM, with an accelerating voltage of 1 keV and an average working distance of 4 mm.
RESULTS AND DISCUSSION

In studying the effects within two-dimensional arrays, two different lattice types were studied. The first array type (Figure 1A) studied was a simulation of the nanosphere lithography (NSL) structure, or Kagome lattice. In traditional NSL, while the in-plane width and out of plane height can be varied, the interparticle distance is fixed for a given in-plane width. Also, there is a lack of control of the defect type and density within the arrays produced. By using electron beam lithography (EBL) this can be overcome, allowing for the study of the coupling distance the NSL structure as well as the effect of defect density. Results for the dark field scattering of the EBL structure as compared to the traditional NSL structure can be seen in Figure 2. The most dramatic effect seen in the EBL produced sample is that the full width half maximum has decreased significantly, due mostly to the lack of defects within the structure. There is also a blue shift in the peak that is due to lack of defects and a non-exact match in particle shape. Excluding the effect of defects on the coupling, we were also able to study the type and effect of the coupling in a perfect NSL array. By varying the interparticle spacing, from 20 nm tip to tip to 1000 nm tip to tip spacing, we were able to see that the coupling in the native NSL structure is at a minimum, with shorter distances having very complex interactions and longer distances acting like isolated nanoparticle. (data not shown)

The second array type seen in Figure 1B is a hexagonal array of disks. These are of interest because they help to paint the full picture in the 1D and 2D coupling theory done by George Schatz and Shengli Zou. [10] Figure 3 is a summary of some of the results obtained for the 2D hexagonal arrays. As can be seen in the results, there is a difference between index matched and non-index matched systems for both the 10x and 60x objectives. In air, there is no shoulder visible or sharpening of the plasmon peak as the spacing approached that of the single particle plasmon peak position. In oil, both a sharpening and a shoulder can be seen for both objectives.

Figure 3. (A) and (B) are the corresponding air and oil scattering spectra for a 10x objective from a Ti array of nanocylinders. (C) and (D) are the corresponding air and oil scattering spectra for a 60x objective.
There are evident diffraction effects, illustrated by the difference in the results for the 10x and 60x objectives. To help elucidate the effects of diffraction on the results, fabrication and testing of Ti arrays were performed. The results are seen in Figure 4. At close spacings, there are strong diffraction effects collected, but as you move to larger spacings, the peak broadens out and becomes more like a background. These peak shapes are in sharp contrast to those observed for the Ag arrays and show that the interactions are more complex than just pure diffraction or plasmonic.

CONCLUSION

In summary, this work provides the first look in more detail at the NSL array utilizing EBL to help understand coupling and defect effects, as well as further studying diffractive coupling effects in other two-dimensional arrays. Critical factors to the success of this experiment are the use of a dark field configuration, a uniform refractive index and high sample quality. By varying the interparticle spacing from 350-800 nm, the diffractively narrowed peak grows into the plasmon spectrum, reaches a maximum and then decreases in intensity and eventually disappears. Also presented are theoretical calculations that support the experimental data. Also presented is the first look at what is seen from a “non” plasmonic array to start to help understand the interactions between the plasmon and diffraction in these unique arrays.

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