Contract No:

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Title of Project
Quantum Fields on Driven Plasmonic Nanostructures

Project Start and End Dates
Project Start Date: October 1, 2020
Project End Date: September 31, 2021

Project Highlights
Meso-scale plasmonic nanoarrays were fabricated using focused-ion-beam techniques (Figure 1). Arbitrary shapes can be drawn in coated films with feature separations as small as 15nm. The electromagnetic scattering behavior of elements within the nanostructures were modeled using finite-dimension-time-domain theory. Model results indicate that light scattering from P-polarized light is primarily from single particle plasmon oscillations (Figure 2). However light scattering from S-polarized light is predicted to be significantly enhanced at longer wavelengths, and that the frequency at peak scattering intensity is greatly influenced by whether particle chains contain even numbers or odd numbers of particles (Figure 3).

Experiments to date have shown some evidence of stable electromagnetic 'domains' of nanoparticles that scatter light from a pump beam. These 'domains' are visible as bright areas in micrographs (Figure 4). They have micrometer size dimensions which is an order of magnitude larger than individual nanoparticles and produce complex scattered light diffraction patterns. The scattered light diffraction patterns are different for S and P polarized light which could result from different electro-magnetic (EM) coupling mechanisms between nanoparticles due to orientation with the polarization of the pump beam. The diffraction patterns of the reflected light beam seem to be independent of pump beam polarization but do shift with the direction of propagation of the pump beam through the nanostructure.

Project Team
Principal Investigator: Patrick O'Rourke - Ph.D. in Physics from Georgia Institute of Technology
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Simona Murph – Ph.D. in Chemistry/Nanotechnology from University of South Carolina
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Binod Rai – PhD in Physics from Rice University
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Michael Thomas – PhD in Chemistry from the University of North Texas
External Collaborators: None

Abstract
Localized Surface Plasmon Resonances (LSPR), generated by the interaction of EM-fields with conductive nanoparticles, are represented as localized coherent quasi-particles which strongly interact with each other and the external environment. These interactions generate non-linear phenomena which can propagate through the nanoparticle structure. These phenomena could be represented as non-local quasi-particles possessing intensity, phase, spin and helicity. This research will explore the physics of non-local effects caused by LSPR interactions in large symmetric nanostructures with the intent of establishing a framework to understand and apply them to plasmonic circuits and sensing devices.

Objectives

This research will investigate the physics of strongly-coupled, highly-symmetric nanoparticle arrays by:

- Adapting mathematical models developed for simpler nanoparticle systems to explore EM-nanoparticle interactions in large assemblies
- Identifying and interpreting model parameters which relate to physical aspects of the nanoparticle assembly and observable effects in EM fields
- Developing techniques to grow nanostructures on suitable optical substrates using self-assembled solution-derived nanocomposites
- Developing techniques to construct large nanostructures on suitable optical substrates using SEM-FIB and e-beam lithography
- Observing and inducing novel EM effects in large nanostructures by introducing local chemical and physical anomalies within the nanostructure.

REVIEWS AND APPROVALS

Authors:

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Intellectual Property Review:

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

SRNL Legal Signature

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Name and Signature

Introduction

Localized Surface Plasmon Resonances (LSPR) are coherent electron oscillations generated by the interaction of EM-fields with conductive nanoparticles. They are represented as localized coherent quasi-particles which strongly interact with each other and the external environment. This interaction is greatly influenced by nanoparticle spacing and geometric arrangement. For small numbers of nanoparticles, it is well studied. But the mechanisms governing the redistribution of energy deposited into a large array of metal nanoparticles is not well understood. This study explores the resonant absorption and scattering of electromagnetic radiation from large scale arrays of gold and silver nanoparticles. These interactions generate non-linear phenomena which can propagate through the nanoparticle structure. These phenomena could be represented as non-local quasi-particles possessing intensity, phase, spin and helicity. This research will explore the physics of non-local effects caused by LSPR interactions in large symmetric nanostructures with the intent of establishing a framework to understand and apply them to plasmonic circuits and sensing devices.

Meso-scale plasmonic nanoarrays were fabricated using focused-ion-beam techniques (Figure 1). Arbitrary shapes can be drawn in coated films with feature separations as small as 15nm. The electromagnetic scattering behavior of elements within the nanostructures were modeled using finite-difference-time-domain (FDTD_MEEP) and Finite Element Method (FEM_NMPBEM) programs. Model results indicate that light scattering from P-polarized light is primarily from single particle plasmon oscillations (Figure 2). However light scattering from S-polarized light is predicted to be significantly enhanced at longer wavelengths, and that the frequency at peak scattering intensity is greatly influenced by whether particle chains contain even numbers or odd numbers of particles (Figure 3).

Light scattering experiments show some evidence of stable electromagnetic 'domains' of nanoparticles that scatter light from a pump beam. These 'domains' are visible as bright areas in micrographs (Figure 4). They have micrometer size dimensions which are an order of magnitude larger than individual nanoparticles and produce complex scattered light diffraction patterns. The scattered light diffraction patterns are different for S and P polarized light which could result from different EM coupling mechanisms between nanoparticles due to orientation with the polarization of the pump beam. The diffraction patterns of the reflected light beam seem to be independent of pump beam polarization but do shift with the direction of propagation of the pump beam through the nanostructure.

Approach

Modeling:

Over 550 simulations were run in total, using two different software packages (MEEP with Python and MNPBEM with Matlab) to calculate the scattering intensity for various arrangements of nanoparticles. These included gold and silver particles, including silica coated, of various sizes and shapes. Simulations included particles arranged in chains with varying gaps or holes, square lattices, rotated lattices, clusters of particles, etc. See Figure 1 for an example of (a) a chain of 5 nano-cubes and (b) a 4x4 square lattice of nano-spheres.

Fabrication:

Dove prisms from Thor Labs (PS990) were used as substrates for gold and silver films. The prisms were cleaned and dried, then coated with a thin layer of chromium to promote adhesion. Approximately 100 nm of gold or silver was then deposited. Nano structures were fabricated in the gold or silver layers using a Zeiss scanning electron microscope with fast ion bombardment (SEM-FIB). The FIB gallium ion source was operated at 30KV and 1picoamp and produced a minimum spot size of 15 nm. The focused ion beam was line-scanned over the gold or silver surface in a cross-hatch pattern with line spacing of 65nm or 100nm. The 100nm spacing left an array of square nanoparticles with ~85nm dimension separated by ~ 15nm gaps. The 65nm spacing left an array of square nanoparticles with ~50nm dimension separated by ~ 15nm gaps. Figure 1 is an SEM image of a 100nm pattern in gold film. Arrays as large as 100 x 100 microns were produced, containing 1,000,000 nanoparticles.

Light Scattering:
Optical radiation was coupled into the nanostructure by directing a beam of light through one of the 45° surfaces of the dove prism. The light is refracted toward the surface supporting the nanostructure and reflected from it by total internal reflection. The reflected beam exits the dove prism through the second 45° surface where it is imaged by a high-resolution camera. Evanescent light which interacts with the nanostructure is scattered into space above the prism and is imaged by a second high-resolution camera.

Accomplishments

Modeling:

- Successfully ran over 550 simulations with MEEP and MNPBEM
  - MEEP uses the finite-difference time-domain method (FDTD) to compute the calculations for the simulations [1]
  - MNPBEM uses a boundary element method (BEM) to compute the calculations for the simulations [2]
- Discovered interesting patterns in the scattering for chains of 50 nm spheres and cubes (see Figure 2, 3, 4 below)
- Studied scattering in broader range of wavelengths than usually investigated (up to 1500 nm)

Fabrication:

- Successfully fabricated mesoscale nanostructures with feature sizes down to 15nm.

Light Scattering:

- Imaged transmitted and scattered light from mesoscale nanostructures
- Demonstrated strong coupling effects in scattered light that are polarization dependent
- Diffraction patterns from nanostructures possibly indicate long range organization

Future Directions

- Investigate further into behavior observed in the simulations, the theory and equations behind the patterns found in the scattering for the 50 nm spheres and cubes
  - Equation for repeated curve in Figure 2 and Figure 3
  - Equations for shift and intensity in Figure 2
  - Cause of differing behavior for odd/even chain lengths, seen in Figure 2 and Figure 4
- Investigate further the surface interactions causing the differences between the cube and sphere nanoparticles
- Simulate diffraction results obtained experimentally, investigate theory and equations
- Measure light scattering as a function of wavelength and polarization
- Investigate possible enhanced Raman and fluorescence spectroscopies from nanostructures surfaces.

FY 2021 Peer-reviewed/Non-peer reviewed Publications

None

Intellectual Property
None

Total Number of Post-Doctoral Researchers
2: Stephanie Gamble and Michael Thomas

Total Number of Student Researchers
0

Figures:

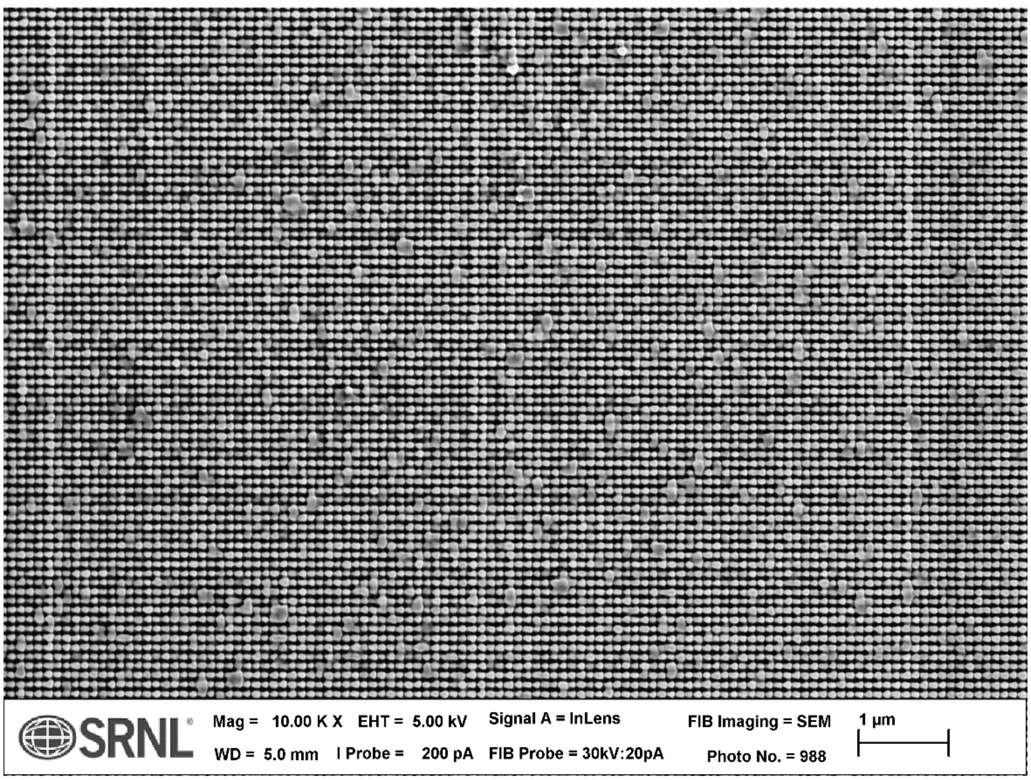


Figure 1: SEM micrograph of 100nm line-spaced square cross-hatch pattern in gold film. Pattern extent is 100 x 100 micrometers. FIB spot size 15nm.

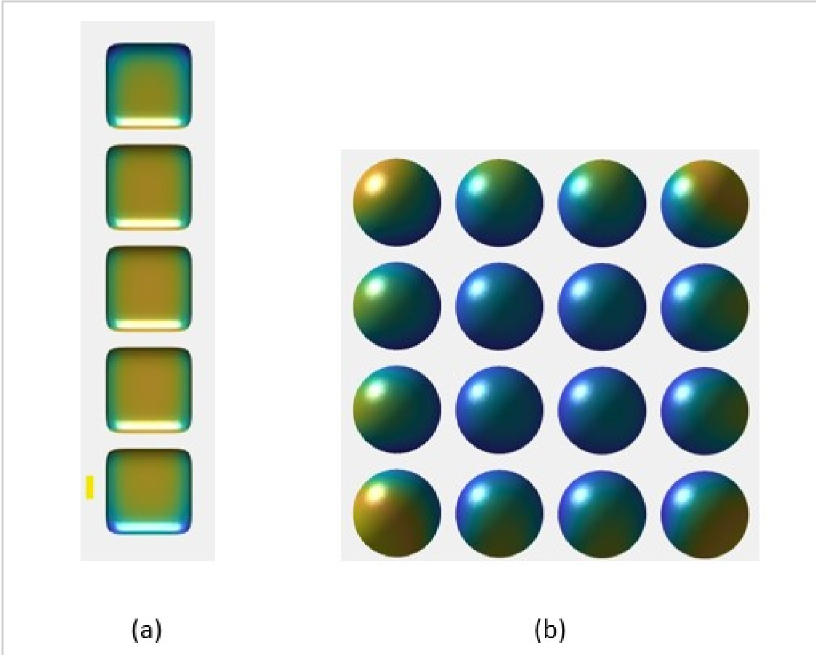


Figure 2: Surface plots of a plasmon mode for (a) a chain of 5 nano-cubes, and (b) a 4x4 square lattice of nano-spheres.

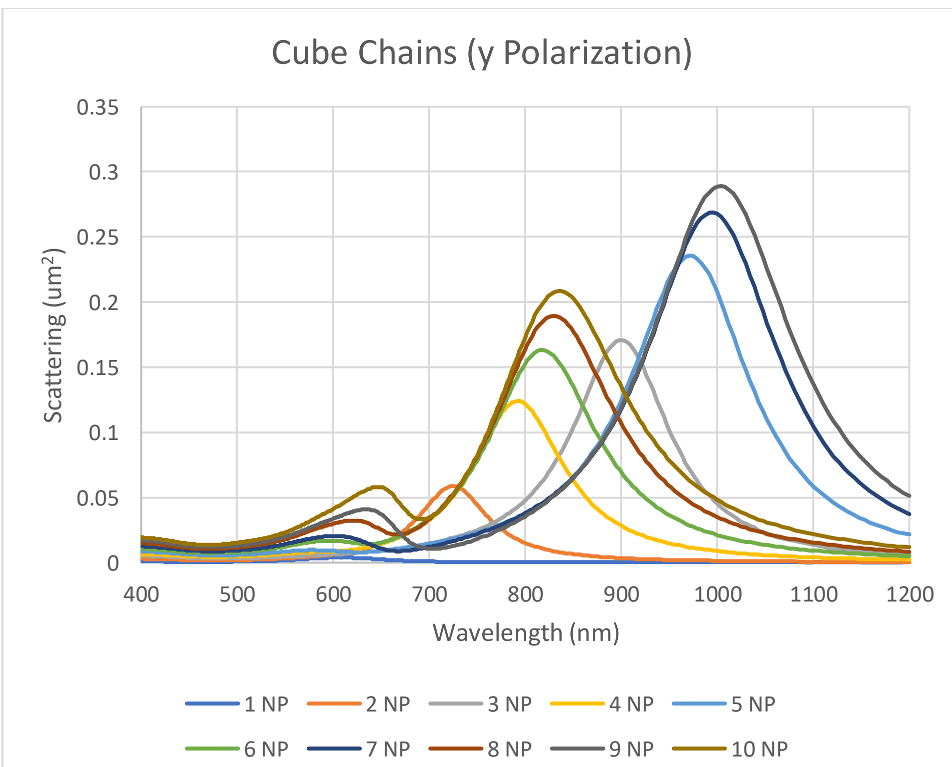


Figure 3: Plot of scattering data for chains of gold cube nanoparticles (polarization in y direction is equivalent to S-type polarization)

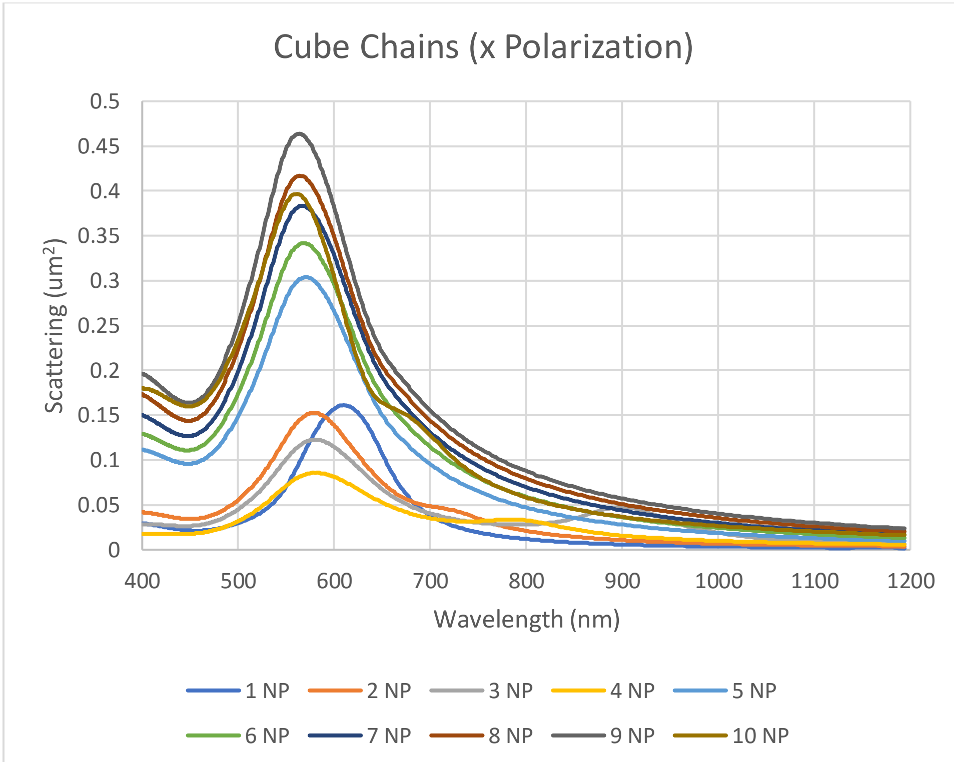


Figure 4: Plot of scattering data for chains of gold cube nanoparticles (polarization in the x direction is equivalent to P-type polarization).

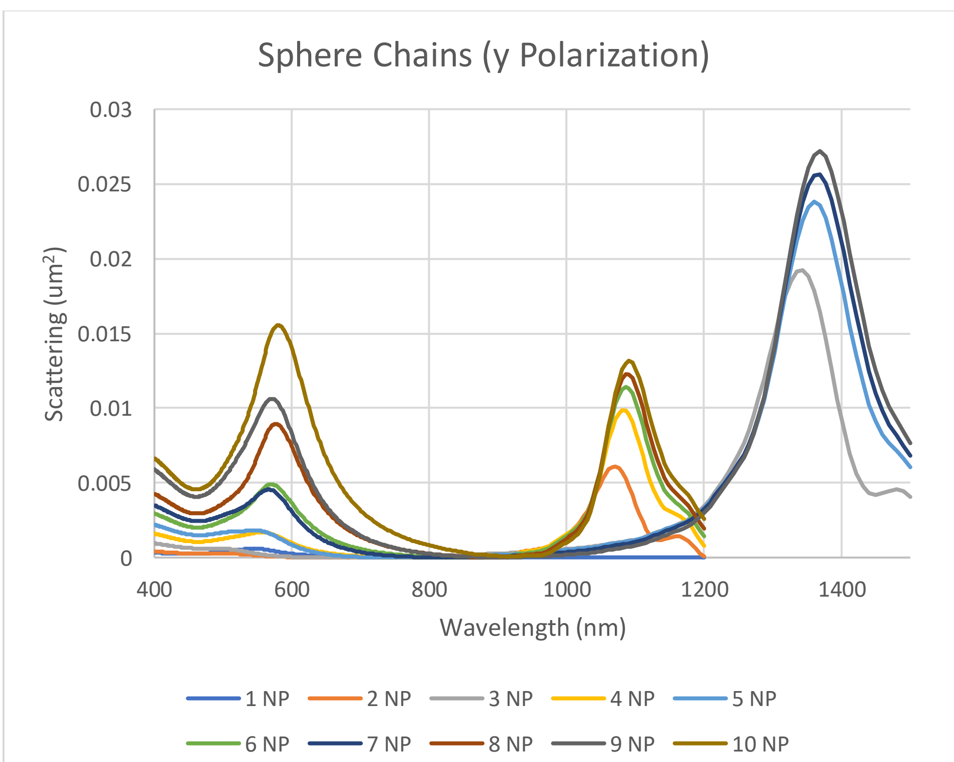


Figure 5: Plot of scattering data for chains of gold sphere nanoparticles (polarization in the y direction is equivalent to S-type polarization).

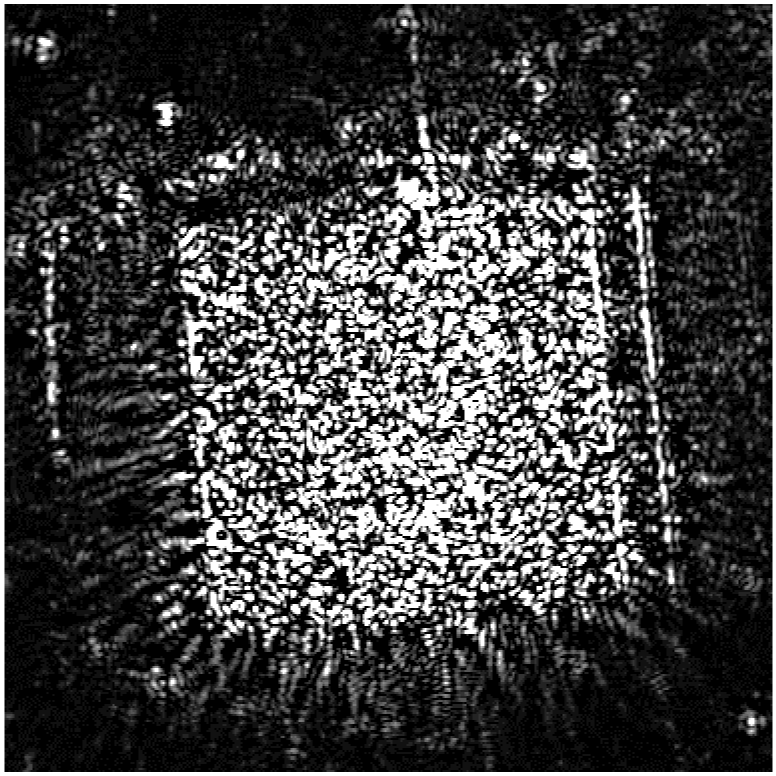
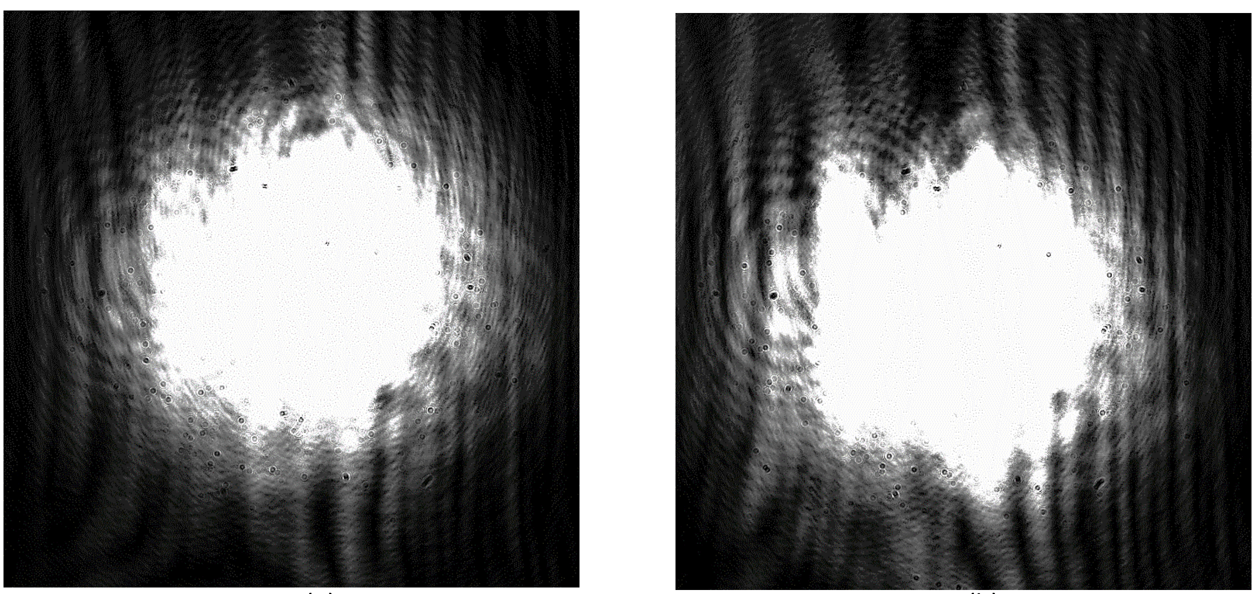
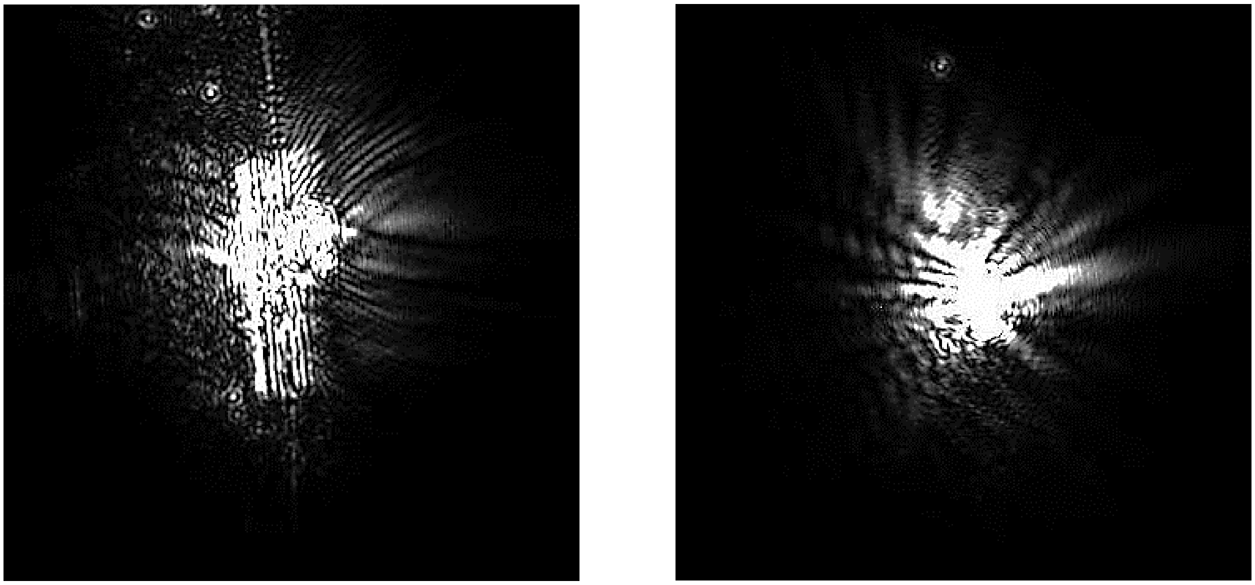


Figure 5. 90° scattered-light image of 25x25 μm gold nanostructure, 65nm line-space square cross hatch. Illumination: 640nm laser, total-internal-reflection.



(a) (b)

Figure 6. Diffraction image of 640nm transmitted light after interaction with nanostructure in figure 5. (a) P-type polarization. (b) S-type polarization



(a) (b)

Figure 7. Diffraction image of 640nm scattered light after interaction with nanostructure in figure 5.
(a) P-type polarization. (b) S-type polarization

References

[1] A. Oskooi, D. Roundy, M. Ibanescu, P. Bermel, J.D. Joannopoulos, and S.G. Johnson, MEEP: A flexible free-software package for electromagnetic simulations by the FDTD method, *Computer Physics Communications*, Vol. 181, pp. 687-702, 2010

[2] U. Hohenester, A. Trügler, MNPBEM – A A Matlab toolbox for the simulation of plasmonic nanoparticles, *Computer Physics Communications*, Vol. 183, No. 2, pp 370-381, 2012