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Infrared Optical Metamaterials

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14. ABSTRACT

This memorandum presents research conducted by Dr. Sarah Brittman (Code 6818) during her Jerome and Isabella Karle Distinguished Scholar Fellowship. It describes the fabrication and preliminary characterization of two new types of infrared metamaterials: 1) binary superlattices of Cu2-xS and PbS colloidal nanocrystals to harness plasmon-exciton coupling in the short-wave infrared and 2) 3D-printed, gold-coated nano-spirals to manipulate the polarization and angular momentum of far-infrared light. Both new material systems allow for their critical parameters to be tuned during fabrication, opening the door to future detailed studies of structure-function properties.

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EXECUTIVE SUMMARY

This report presents research conducted by Dr. Sarah Brittman (Code 6818) during her Jerome and Isabella Karle Distinguished Scholar Fellowship from May 11, 2020–May 10, 2021. It details the fabrication and preliminary characterization of two new types of infrared metamaterials: 1) binary superlattices of $Cu_{2-x}S$ and PbS colloidal nanocrystals to harness plasmon-exciton coupling in the short-wave infrared and 2) 3D-printed, gold-coated nano-spirals to manipulate the polarization and angular momentum of far-infrared light. Both new material systems allow for their critical parameters to be tuned during fabrication, opening the door to future detailed studies of structure-function properties in these new materials.

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INFRARED OPTICAL METAMATERIALS

1. INTRODUCTION

Manipulating light-matter interactions at the nanoscale has the potential to create materials with properties that go beyond those achievable in natural materials. For example, such materials can exhibit exotic phenomena such as negative index of refraction [1], epsilon near zero [2], or hyperbolic dispersion [3]. These metamaterials have potential applications in DoD-relevant fields such as chemical sensing, quantum information, photonic circuits, photodetection, and imaging. The invisible, infrared region of the electromagnetic spectrum is of particular value to the DoD, so the work conducted during this Karles Fellowship has focused on two specific types of new metamaterials (**Fig. 1**):

1. Binary superlattices of $Cu_{2-x}S$ and PbS colloidal nanocrystals to harness plasmon-exciton coupling in the short-wave infrared and

2. 3D-printed, gold-coated nano-spirals to manipulate the polarization and angular momentum of far-infrared light

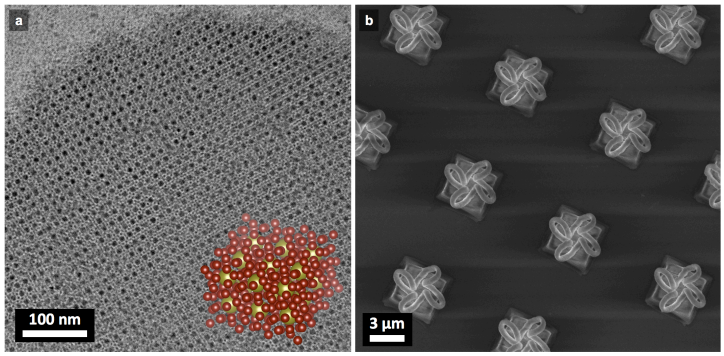

Fig. 1: Examples of the two new materials that were investigated. a) Transmission electron microscopy (TEM) image of a colloidal nanocrystal binary superlattice of PbS and $Cu_{2-x}S$ nanocrystals. Inset is a diagram of its structure that is analogous to the atomic crystal structure of $NaZn_{13}$. PbS nanocrystals are shown in gold and $Cu_{2-x}S$ nanocrystals in red. b) Scanning electron microscopy (SEM) image of an array of 3D-printed 4-loop nano-spirals before coating with gold.

Manuscript approved June 14, 2021.

2. EXPERIMENTS

2.1 Binary superlattices of $Cu_{2-x}S$ and PbS colloidal nanocrystals

2.1.1 Motivation

Semiconductor nanocrystals are called "artificial atoms" because their physics shows striking parallels with atomic physics. Similar to the way natural atoms form a crystal, these nanocrystal "atoms" self-assemble into ordered, three-dimensional superlattices. Because nanocrystals are much smaller than the wavelength of light, superlattices that integrate nanocrystals of different properties (e.g., metals, semiconductors, dielectrics, and magnetic materials) have the potential to generate new light-matter interactions that are not achievable in natural materials [4]. Nanocrystal superlattices formed by self-assembly are an alternative to the top-down techniques most often used to fabricate such metamaterials and can create complex three-dimensional lattice structures relatively simply. These superlattices can be constructed from a single type of nanocrystal or from two different types of nanocrystals, which are known as binary superlattices.

For applications, binary superlattices are particularly interesting because they unite complementary functionalities, such as localized surface plasmons and light emission, within the same material. The diameters and carrier concentrations of the nanocrystals allow these excitations to be tuned in and out of resonance, offering a controllable way to study coupling between these excitations within the metamaterial. Such plasmonic-excitonic materials could find applications in enhancing the efficiency of infrared photodetectors or creating nanoscale infrared light sources, such as spasers.

Infrared photodetectors made from disordered films of colloidal PbS nanocrystals are already available commercially at much lower cost than competing InGaAs technology. They also have the potential to push detection deeper into the short-wave infrared, beyond 2 μm. Superlattices of such nanocrystals are the next frontier for improving the performance of this new class of photodetectors.

2.1.2 Results

I assembled the first binary superlattices from infrared plasmonic $Cu_{2-x}S$ and excitonic PbS nanocrystals [5]. Previously $Cu_{2-x}S$ had been incorporated only into single-component superlattices. Superlattices were assembled from the same parent solution both on TEM grids for imaging and on silicon substrates for correlated grazing-incidence small-angle X-ray scattering (GISAXS) analysis of their lattice spacings, symmetries, and grain sizes. The relative concentrations of the two component nanocrystals were varied to generate a variety of binary phases within each system. First, binary superlattices from large PbS and small $Cu_{2-x}S$ nanocrystals were assembled, with structures bearing stoichiometries of AB_{13}, AB_4, AB_3, AB_2, and AB, where A is the larger PbS and B is the smaller $Cu_{2-x}S$ nanocrystal.

Our team also developed a new chemical process for modifying the surface chemistry of large $Cu_{2-x}S$ nanocrystals by adding a thin (~0.9 nm) PbS shell [6]. This shell enhanced the solubility of the $Cu_{2-x}S$ nanocrystals, allowing us to assemble binary superlattices of large $Cu_{2-x}S$ and small PbS nanocrystals. This surface treatment had the additional benefit of blue-shifting and intensifying the plasmonic band of the $Cu_{2-x}S$ nanocrystals, which was correlated to a change in crystal structure of the $Cu_{2-x}S$ induced by the addition of the PbS shell. Photoluminescence measurements of our binary nanocrystal systems indicate that a chemical interaction between the $Cu_{2-x}S$ and PbS nanocrystals quenches the emission of the PbS nanocrystals when mixed in concentrated solution, which is an essential step for the formation of the superlattices; however, the PbS shell on our $Cu_{2-x}S$/PbS nanocrystals prevents this effect and allows the assembly of binary superlattices without full quenching of the PbS

photoluminescence [5,6]. The surface modification process and its enabling of optically active binary superlattices of $Cu_{2-x}S$/PbS and PbS nanocrystals are the subject of U.S. Patent Application #17238265 filed on April 23, 2021 [7].

2.1.3 Conclusions and future directions

These superlattice structures are a first step toward understanding how infrared plasmons and excitons couple within three-dimensional superlattice metamaterials generated by relatively simple self-assembly. The ability to tune the binary phases, and therefore the coupling distance and nearest neighbors between the plasmonic and excitonic nanocrystals, offers a platform for future studies of infrared plasmon-exciton optical coupling at the nanoscale. Future work will focus on increasing our control over the specific lattices that are formed and their domain size, with the goal of increasing the domains to several micrometers. Such domains are then suitable for single-domain optical measurements in our new scanning optical microscope, which was installed in December 2020.

To that end, I modified our commercial microscope, enabling it to perform quantitative reflectance and transmittance measurements from 450-1620 nm, on the length scale of ~2-3 um (**Fig. 2**). The system was validated on control samples such as silicon and films of PbS nanocrystals that were calibrated first over large areas using our commercial UV-visible spectrophotometer. I also purchased a calibration light source that fits in our new microscope to measure the response function of our optics. Measuring the calibration curves allows us to remove instrumental artifacts from our collected photoluminescence spectra (**Fig. 3**).

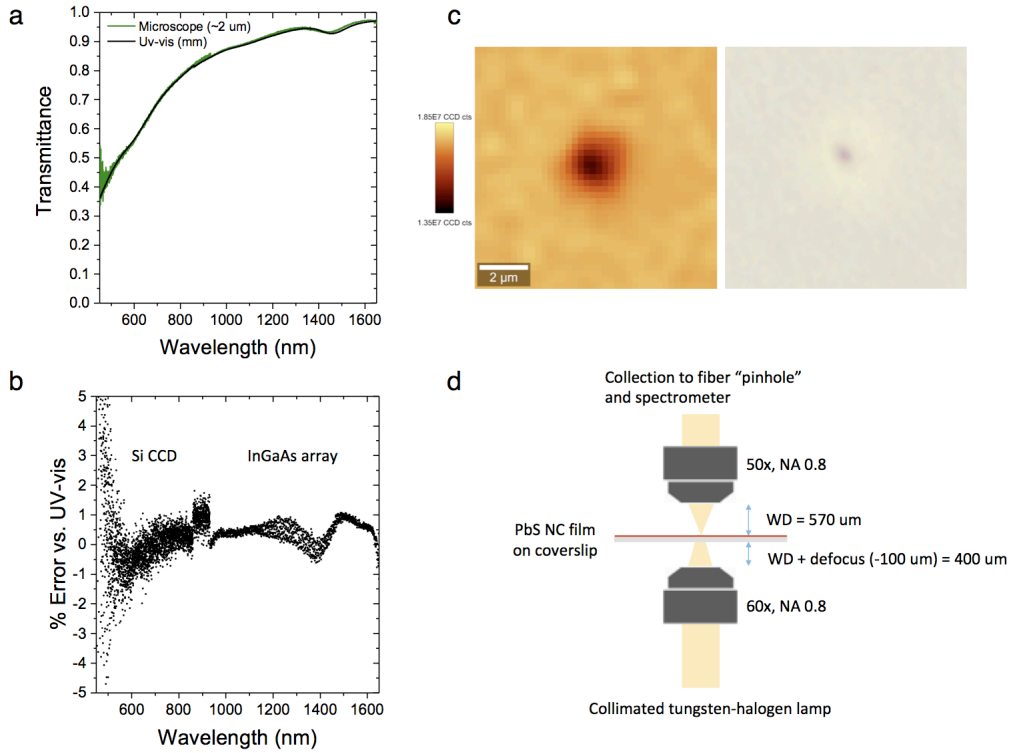

Fig. 2: Validation of our micro-transmittance measurement setup. a. Transmittance from a PbS nanocrystal film measured using a commercial UV-visible spectrophotometer (black line) and our microscope (green line). b. Percent error of the micro-transmittance measurement referenced to the spectrophotometer. c. Spatially resolved counts of transmission of a defect in the PbS film showing the spatial resolution of a few micrometers. d. Schematic of the micro-transmittance measurement.

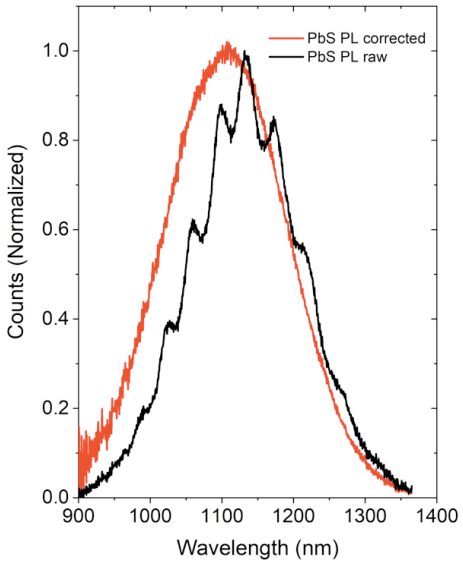

Fig. 3: Raw photoluminescence spectrum (black) and corrected spectrum (red) after calibration of the microscope.

Combining our binary superlattices with our new microscopic characterization instrument will allow us to probe the optical signatures of exciton-plasmon coupling within these new infrared materials.

2.2 3D-printed, gold-coated nano-spirals

2.2.1 Motivation

3D nanolithography offers a way to design and control the optical response of nanoscale materials in a third dimension, previously inaccessible by traditional 2D lithographic techniques. This approach is particularly powerful for creating spiral structures that are expected to couple to the spin or orbital angular momentum of incident photons, yielding a new way to manipulate these additional characteristics of light [8]. Such control could find applications in the sensing and identification of chiral molecules, activation of optical transitions in materials typically forbidden by angular momentum selection rules, phase-structured light sources, or polarization and orbital angular momentum-multiplexed optical communications. One drawback of current 3D nanolithography techniques based on two-photon polymerization is that the spatial resolution is limited to the 2-photon spot size, typically ~300 nm, so new strategies must be developed to decrease this feature size. Achieving smaller features will extend the bandwidth over which the new materials are optically active and open up new opportunities for manipulating spin and orbital angular momentum.

2.2.2 Results

A commercial nanoscale 3D printing tool (Nanoscribe GT Professional) was used to fabricate spiral structures from a commercial photoactive polymer (IP-DIP). An annealing protocol was developed to carbonize and shrink the polymer nano-spirals in size. Then the shrunken nano-spirals were coated with a 35-nm shell of gold using thermal evaporation to enhance their interaction with light.

Nano-spirals were successfully reduced in size by developing a slow heating and cooling protocol. The nano-spirals were loaded into a quartz tube within a tube furnace under Ar atmosphere and ramped at 2°/hr to their final temperature. After being held at this temperature for 30 minutes, the samples were left to cool gradually to room temperature before being removed from the furnace. By varying the final temperature from 350-500°C, the amount of shrinkage in the nanostructures was controlled (**Fig. 4**). Higher temperatures tested with this same protocol (above 700°C) destroyed the nanostructures; however, further size reduction might be possible in the future using a more inert atmosphere within the annealing tube – for example by pumping and purging with Ar to remove trace amounts of oxygen.

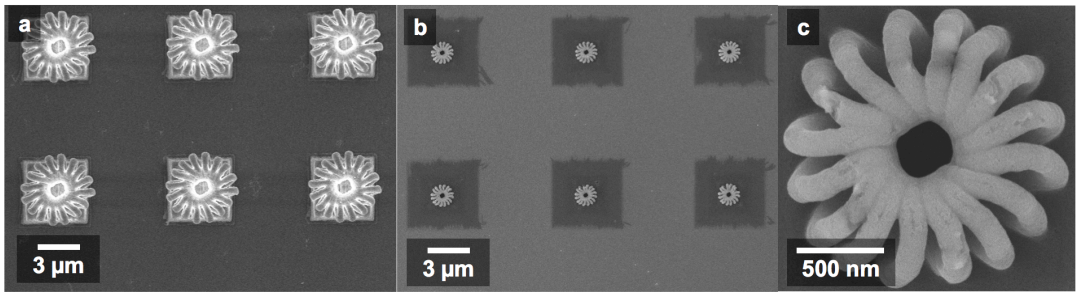

Fig. 4: The shrinking of 16-loop nano-spirals. SEM images of nano-spirals as fabricated (a), and shrunk to 33% of their original size (b,c).

To determine their structure-function properties, the reflectance of arrays of these nano-spirals was measured under unpolarized light and referenced to the surrounding Au-coated silicon substrate (**Fig. 5**). Samples were measured using a Bruker Vertex 80v FT-IR spectrometer and Hyperion microscope purged

with N_2 and equipped with a 15x NA 0.4 reflective objective and liquid nitrogen cooled Mercury-Cadmium-Telluride (MCT) detector. As-made nano-spirals show sharp peaks in the low energy region (500-2000 cm^{-1}) from vibrations in the polymer (**Fig. 5a**). Annealing treatments used to shrink the nano-spirals carbonize the polymer, reducing these interfering peaks. Periodic oscillations clear in the higher energy region of the spectra (3500-6000 cm^{-1}) for larger nano-spirals suggest scattering to an in-plane lattice resonance that shifts to higher energies as the spacing between the nano-spirals in the array decreases from 10 to 6 µm (**Fig. 5b**). These oscillations are not visible in the smallest nano-spirals with the same 6-µm periodicity (**Fig. 5c**), likely because of the greatly reduced scattering cross-section of the smaller structures. These smallest nano-spirals show the most intriguing behavior: moving from the 20-loop spiral to fewer loops, the resonance is at first a single broad peak that then splits into two separate peaks, clearest in the 12- and 8-loop spectra. The geometric origin of this peak splitting will be the subject of future work.

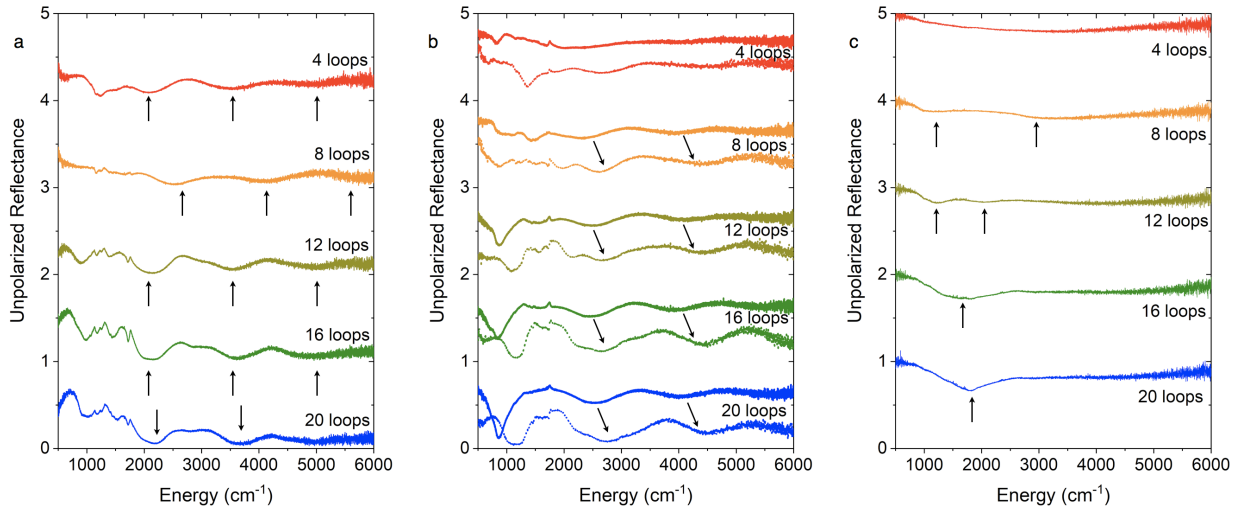

Figure 5: Mid- and long-wave infrared unpolarized reflectance spectra of gold-coated nano-spirals. Spectra are vertically offset by 1 for clarity. a) As-made nano-spirals with periodicity of 6 µm. Arrows indicate the periodic oscillations. b) Nano-spirals shrunk to 63% of their original size with periodicities of 10 µm (top curve of each pair) and 6 µm (bottom curve of each pair). Arrows indicate the blueshift of the periodic oscillations. c) Nano-spirals shrunk to 33% of their original size with 6 µm periodicity. Arrows indicate the broad resonance (20 loops) that splits into two resonances as the number of loops is reduced.

2.2.3 Conclusions and future directions

While preliminary structure-property relationships have been investigated, polarization-dependent optical measurements are the next step for more thoroughly understanding how these nano-spirals interact with light. Interferometry will then be necessary to confirm the nano-spirals' interaction or generation of light with orbital angular momentum. Full-wave electromagnetic simulations are anticipated to provide insight into the nature of the resonances observed in various regions of the spectra and their relationship to the geometric attributes of the spirals and their lattice arrangement. Such analysis will allow the determination of design rules for achieving desired coupling of these nano-spirals to spin and orbital angular momentum of light.

3. SUMMARY

The creation of these two new materials systems has laid the groundwork for further understanding and control of their properties. Both new material systems allow for their critical parameters to be tuned during fabrication, opening the door to future detailed studies of structure-function properties. In the future, further experimental characterization will be combined with full-wave electromagnetic simulations to interpret these properties and develop design rules for tailoring the materials to specific applications. I have also developed new microscopic tools for measuring local material properties that will be invaluable in evaluating the structure-property relationships and uniformity of new optical materials.

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