LABORATORY DIRECTED RESEARCH AND DEVELOPMENT

PROPOSAL TITLE: SYNTHESIS AND CHARACTERIZATION OF HIGH-FREQUENCY MAGNETIC METAMATERIALS FOR TUNABLE LIGHT HARVESTING AND EMISSION

LEAD SCIENTIST:	JENNIFER A. DIONNE
Phone:	650-736-2286
Email:	jdionne@stanford.edu
Date:	April 15, 2011
Department/Division/ Directorate:	SIMES/PSD
Other Scientists:	
Proposal Term	**From: 10/2011** **Through: 09/30/2014**

Business Manager:	Nancy Matlin
Phone:	650-9266232
Email:	matlin@slac.stanford.edu

SLAC-LDRD-0026-12

Published By:

SLAC National Accelerator Laboratory
2575 Sand Hill Road
Menlo Park, CA 94025

Abstract

We propose to design and characterize a suite of engineered bulk materials exhibiting high-frequency magnetism with permeabilities spanning large positive and negative values throughout optical and ultraviolet wavelengths. We will use these materials for wavelength and subwavelength light energy harvesting and emission, focusing on development of high efficiency solar collectors and microscale free electron light sources.

Summary of Proposal

Description of Project

Controlling light-matter interactions across wavelength and subwavelength scales holds substantial promise for novel electromagnetic phenomena and applications. Fundamentally, these interactions are determined by a material's permittivity and permeability – intrinsic material properties that describe the response of charges and currents to an applied electromagnetic field. Above optical frequencies, most natural materials are non-magnetic and are characterized by a unity permeability. However, if the sign and magnitude of the permeability could be tuned at will, the propagation of light or electrons could be controlled in unprecedented ways. Among the many enabling applications of designer permeabilities (and hence refractive indices) are sub-diffraction-limited lenses [1], efficient light or solar concentrators [2], optical nanoantennas [3], electromagnetic cloaks [4], and microscale free electron light sources [5]. While these applications have been realized at microwave and infrared frequencies, metamaterials could have profound impact for the DOE if the operating frequency could be scaled to the visible range or even ultraviolet and x-ray frequencies. In this proposal, we will develop a suite of visible and ultraviolet frequency magnetic metamaterials with large positive and negative permeabilities. Specific aims of this proposal include: 1) design and synthesis of such magnetic metamaterials using full-field analytic calculations and colloidal assembly; 2) electromagnetic characterization of magnetic metamaterials with nanometer-scale resolution using optical microscopy and electron energy loss spectroscopy; and 3) application of magnetic metamaterials to solar energy collection and free-electron light emission. Our investigation of these novel materials will use the facilities in Stanford's NanoCenter and in the SIMES research labs at SLAC.

Expected Results

Our investigation of magnetic metamaterials will lead to new materials with designer permeabilities and permittivities across a broad range of visible and ultraviolet wavelengths, which can potentially be scaled to x-ray frequencies. Since strong magnetic resonances do not naturally occur for these higher photon frequencies, the results will have broad impact on research fields requiring tunable light-matter interactions on both wavelength and subwavelength scales. Our proposal will focus on development of next-generation solar energy-harvesting devices and free-electron light emission using these magnetic metamaterials.

Proposal Narrative

Purpose/Goals

The goal of this proposal is to design, develop, and characterize novel metamaterials exhibiting a strong magnetic response at visible and ultraviolet frequencies. These metamaterials will enable unprecedented tunability of a material's permeability, which in turn enables precise control over light-matter and electron-matter interactions on subwavelength scales. In particular, these materials can enhance the local electromagnetic field strengths by orders of magnitude, leading to reduced optical power requirements by the field enhancement factor. Such novel material development is well-aligned with SLAC's mission to "explore the ultimate structure and dynamics of matter and the properties of energy," in this case yielding a completely new class of materials for light harvesting and emission. Ultimately, we will apply these metamaterials to two problems of critical importance to the DOE: 1) the development of high efficiency solar-energy collectors and concentrators and 2) development of a microscale free electron light source.

Approach/Methods

Our metamaterials are composed of nanoscale metal and dielectric resonators that serve as "artificial atoms" of our material. Figure 1 illustrates two proposed nanoresonator geometries that will enable high-frequency magnetism, including a small metal-coated dielectric nanocrescent and a close-packed cluster of

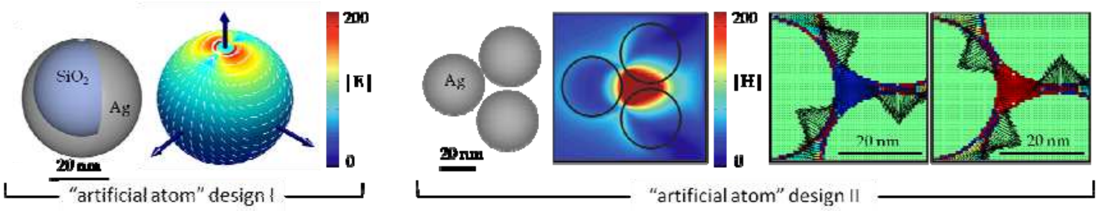

Figure 1: Nanoresonator or "artificial atom" geometries for high-frequency magnetic metamaterials. Design 1 is composed of a nanocrescent that supports a strong dipole moment (color scale) which induces circulating displacement currents (white arrows), leading to a magnetic dipole. Design 2 is composed of three closely spaced nanoparticles which can also induce circulating displacement currents and a magnetic dipole. The right-most images plot time-snapshots of the magnetic field (color scale) and displacement current (arrows). As plotted, each geometry supports magnetic mode exists for wavelengths in the red, though tunability to the blue or ultraviolet is possible through scaling the resonator dimensions and material indices.

metallic nanoparticles. We have already developed the computational framework for exploring the modes of these metamaterials, and have theoretically demonstrated their visible-frequency magnetic and electric resonances [6,7]. Figure 1 illustrates the near-field electric and magnetic field profiles as well as the displacement currents supported by these nanoresonator geometries. In both the crescent and cluster geometries, displacement currents circulate around the "artificial atom" at specific, tunable optical frequencies, giving rise to a strong magnetic field in the core which can be over 200x that of the incident electromagnetic field. The resultant magnetic dipole moments give rise to magnetic permeabilities that significantly deviate from 1 and can even be negative at optical frequencies.

<u>Synthesis:</u> We propose self-assembly to create the nanocrescent magnetic metamaterials of Figure 1(I) and DNA-directed assembly to create the metamaterial nanoparticle clusters of Figure 1(II). In both cases, "artificial atom" synthesis will be characterized with a combination of tools available at Stanford and SIMES including ultraviolet-visible spectroscopy, transmission electron microscopy, and small angle x-ray scattering.

I. Crescent-based metamaterials: Crescent synthesis will begin with a 30-50 nm polymeric nanoparticle on a resist substrate. The polymeric nanoparticle can be coated in a variable-thickness metal to form the crescent shell through an angled evaporation on a rotation stage. After coating, the particles can be lifted off the resist substrate by dissolution of the resist. Individual nanocrescents have already by synthesized by L. Lee at Berkeley for applications in surface-enhanced Raman spectroscopy. [8] We will fabricate periodic arrays of crescents using a combination of self-assembly and PDMS stamping to achieve control over the inter-crescent spacing and crescent orientation. [9]

II. Cluster-based metamaterials: Metallic nanoparticles can be synthesized by controllably reducing a metal ion salt in solution with a stabilizing ligand. We will use DNA-directed assembly to achieve the small interparticle separations (~2 nm) necessary to induce visible and ultraviolet magnetic resonances. Following nanoparticle synthesis, the nanoparticles will be immersed in equimolar amounts of thiolated DNA which can exchange with the as-synthesized ligands. Thereafter, gel electrophesis will be used to systematically purify particles with one attached DNA strand. This procedure will be repeated on multiple nanoparticle solutions to obtain batches with unique DNA handles. The nanoparticle solutions will then be combined together with a longer template DNA strand that will interweave each single-particle - single-DNA conjugate via complementary base-pairings to achieve the desired cluster geometry.

Electromagnetic characterization: The electromagnetic properties of our "artificial atoms" will be explored using both far-field optical microscopy and scanning transmission electron energy loss spectroscopy. For optical characterization, isolated "artificial atoms" will be dispersed on a substrate and excited with coherent monochromatic or supercontinuum illumination. Dark-field microscopy will be used to probe scattering and extinction spectra of these artificial atoms. Cross-polarization microscopy will be used to determine the electric and magnetic polarizabilities throughout visible and ultraviolet frequencies. Electron energy loss spectroscopy in a scanning transmission electron microscope will be used to map the electromagnetic modes of these "artificial atoms" with nanometer-scale resolution. In combination with electron holography and tomography, we will create three-dimensional profiles of the electric and magnetic fields in these structures throughout visible and ultraviolet frequencies. We will also characterize the properties of bulk magnetic metamaterials composed of our artificial atoms arranged in a periodic lattice. Measurements of the amplitude and phase of the reflected and transmitted light can be used to extract the permittivity and permeability of the metamaterial as a function of frequency. Similarly, refraction experiments through a thin layer of the metamaterial will be performed to derive the effective refractive index.

Applications: We propose applying these metamaterials to two specific research areas of critical importance to the DOE and to SLAC, namely solar energy

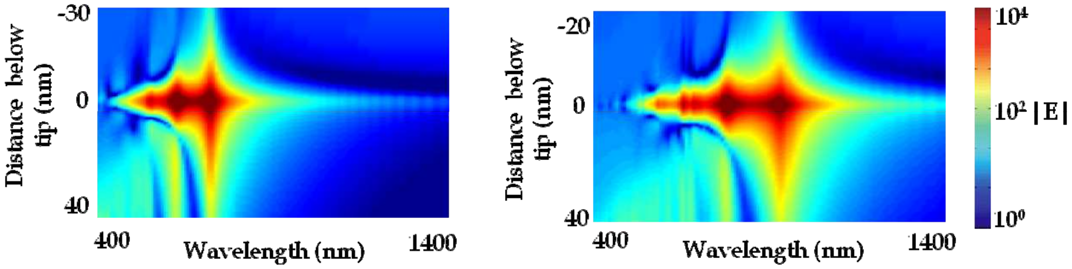

Figure 2: Near-field spectra of individual nanocrescents for various positions above and below the crescent tips. Broadband field enhancements exceeding 10 can be seen throughout the entire dielectric core. Further, the resonance wavelengths can be blue or red-shifted based on the core refractive index, tip-spacing, or crescent size. On the left, the core has an index of 1.5; on the right, the core has in index of 2.

concentration and free electron light emission. Both applications rely on the unique opportunity to tune the permeability and permittivity with these metamaterials and hence create new optical elements that cannot be achieved with natural materials (i.e., impedance-matched layers for solar cells, new mirrors for ultraviolet and potentially x-ray frequencies, novel nanoantennas for directional light emission). For example, the proposed crescent-based metamaterials enable enhanced light absorption across a broad range of visible frequencies throughout the core of the nanocrescent, as shown in Figure 2. Compared to the incident light, intensity enhancements within the nanocrescent exceed at least 10. We propose patterning a close-packed array of nanocrescents as the back contact of a poorly absorbing solar cell, such as an organic or nanocrystalline solar cell. The crescent interior will be infiltrated with the cell semiconducting active media to enhance absorption and improve the device performance. Likewise, magnetic metamaterials may provide a particularly promising route towards development of a tunable, highly efficient micro- or nanoscale free electron light source for visible and ultraviolet wavelengths. The concept is based on recent results demonstrating that a nanoscale periodically-layered planar metal-dielectric structure creates a tunable, incoherent radiation source [5] whose intensity can be enhanced by coupling to magnetic modes [10]. This “light well” emits photon wavelengths between 700 nm and 900 nm for electron energies of 20-40 eV. AC electric and magnetic resonances in these structures would not only enhance the field concentration and hence the emitted electromagnetic intensity, but may allow the fields excited by the electrons to interfere constructively, producing a coherent electron light source. We will use cathodoluminescence spectroscopy to quantify the emission enhancement in these metamaterial-based free electron sources.

Specific Location of Work

Synthesis and characterization will be performed in SIMES ("artificial atom" synthesis), at Stanford in the Durand Building, Room 190 (DNA-directed assembly and optical characterization), and in the Stanford Nano Center (electron beam excitation and characterization of electric and magnetic resonances using a combination of EELS, holography, and tomography).

Anticipated Outcomes/Results

This proposal will result in development of a new class of materials exhibiting a strong magnetic response at high frequencies for novel optical elements (i.e., lenses, concentrators, emitters) in the visible and ultraviolet. Our theoretical calculations will guide metamaterial synthesis, which will be accomplished through a combination of self-assembly and DNA-directed assembly. Optical and electron spectroscopy will be used to characterize our metamaterials. These materials will be used for enhanced solar energy collection and free-electron light emission. Ultimately, the results can be scaled to even higher-frequency metamaterials for precise optical signal control in the extreme-ultraviolet or x-ray regime.

References

1. J. B. Pendry, Negative Refraction Makes a Perfect Lens, *Phys. Rev. Lett.* 85, 3966 (2000)
2. A. Aubry, D. Lei, A. Fernandez-Dominguez, Y. Sonnefraud, S. Maier, and J. B. Pendry, Plasmonic light-harvesting devices over the whole visible spectrum. *Nano Letters* 10, 2574 (2010)
3. N. A. Mirin, N. J. Halas. Light-Bending Nanoparticles. *Nano Letters* **2009**, *9*, 1255-1259.
4. W. Cai, U. Chettiar, A. Kildishev, V. Shalaev, Optical cloaking with metamaterials. *Nature Photonics* 1, 224 (2007)
5. G. Adamo, K. F. MacDonald, Y. H. Fu, C.-M. Wang, D. P. Tsai, F. J. García de Abajo, and N. I. Zheludev, Light well: A tunable free-electron light source on a chip, *Physical Review Letters*, 103, 113901 (2009)
6. S. Sheikholslami, A. Garcia, and J. Dionne, Fano resonances in colloidal metamaterials, in preparation
7. A. Garcia, A. Atre, and J. Dionne, Broadband absorption and density of states in optically-magnetic nanocrescents, in preparation
8. Y. Lu, G. L. Liu, J. Kim, Y. X. Mejia, and L. P. Lee, *Nano Letters*, **5**, 119 (2005).

9. Yu Zhang, Aoune Barhoumi, J. Britt Lassiter, Naomi J. Halas. Orientation-Preserving Transfer and Directional Light Scattering from Individual Light-Bending Nanoparticles. *Nano Lett*. Article ASAP.
10. D. Li, M. Hangyo, Z. Yang, M. R. Asakawa, S. Miyamoto, Y. Tsunawaki, K. Takano, and K. Imasaki, Smith-Purcell radiation from a grating of negative index material, Nuc. Instr. and Methods in Phys. Research, 637, 135 (2011)

VITA (Lead Scientist)

Jennifer A. Dionne, Principal Investigator
Assistant Professor, Stanford University
Department of Materials Science and Engineering
Durand Building, Room 125, 496 Lomita Mall, Stanford, CA 94305
Tel (650) 736-2286; Fax (650) 725-4034; email: jdionne@stanford.edu

Education and Training

2009-2010: Postdoctoral Fellow, University of CA, Berkeley and Lawrence Berkeley National Labs

2009: Ph.D., Applied Physics, California Institute of Technology, Pasadena, California

2005: M.S., Applied Physics, California Institute of Technology, Pasadena, California

2003: B.S., Physics, Washington University in St. Louis, St. Louis, Missouri

2003: B.S., Systems & Electrical Engineering, 2003, Washington University in St. Louis, St. Louis, Missouri

Major Honors and Awards

Stanford:
- Air Force Office of Scientific Research Young Investigator Grant, 2010
- Frederick E. Terman Fellow, Stanford University, 2010-2014
- Robert N. Noyce Family Faculty Fellow, Stanford University, 2010-2014

Caltech:
- Francis and Milton Clauser Prize for best Caltech Ph.D. thesis, 2009
- Materials Research Society Gold Award, 2008
- Everhart Lecturer, Caltech, 2008
- Kavli Nanoscience Institute Graduate Award Winner, 2005
- National Science Foundation Graduate Research Fellow, 2007-2009
- National Defense Science and Engineering Fellow, 2004-2007

Washington University:
- The Tau Beta Pi outstanding student award, 2003

The Systems & Electrical Engineering outstanding student award, 2003
The ODK outstanding student award for campus and community service

Research and Professional Experience

- **Stanford University, Assistant Professor of Materials Science and Affiliate Faculty of the Precourt Institute for Energy (2010 - present)**
  Principal Investigator of a team of 6 Ph.D. students and 3 postdoctoral fellows interested in exploring the fundamental electrodynamic properties of metamaterials and their applications to bioimaging and solar energy harvesting. Professor for "Materials Chemistry" and "Electronic Materials Engineering"
- **University of CA, Berkeley and Lawrence Berkeley National Labs(2009-2010)**
  Postdoctoral fellow in the laboratory of Professor Paul Alivisatos, investigating the optical and electronic properties of single nanoparticle hydrogen-evolving photocatalysts.
- **California Institute of Technology (2003-2009)**
  Graduate student in the laboratory of Professor Harry Atwater, investigating passive and active plasmonic devices, including negative refractive index materials and subwavelength plasmonic modulators.

Selected Publications, Patents, and Press

- 2 patents on plasmonic modulators and color displays
- 11 journal publications with over 600 combined citations; 5 papers in preparation; 1 book chapter
- Text book in preparation, "Introduction to Solar Photonics"
- Work featured in Michio Kaku's book "Physics of the Impossible" and C. Pickover's book "From Archimedes to Hawking: Laws of Science and the Great Minds behind Them."

[1] A. Atre and J. Dionne, "Realistic upconverter-enhanced solar cells with non-ideal absorption and recombination efficiencies", submitted

[2] M. L. Tang, N. L. Liu, J. Dionne, and A. P. Alivisatos, "Observations of shape-dependent hydrogen uptake trajectories at the single nanocrystal level", submitted

[3] J. Dionne, L. Sweatlock, M. Sheldon, A. P. Alivisatos, and H. Atwater, "Si-based plasmonics for on-chip photonics," Journal of Selected Topics in Quantum Electronics, 16, 295 (2010)

Most accessed IEEE article for March 2010

[4] K. Diest, J. Dionne, M. Spain, and H. Atwater, "Tunable color filters based on metal-insulator-metal resonators," *Nano Letters* 9, 2579 (2009)

Featured in Nature Photonics 3, 426 (2009) "Compact colour filters"

[5] J. Dionne*, K. Diest*, L. Sweatlock, and H. Atwater, "PlasMOStor: a metal-oxide-silicon field-effect plasmonic modulator", *Nano Letters* 9, 897 (2009) (*equal-author contributors)

Featured in Science News, fall 2009

[6] J. Dionne, E. Verhagen, A. Polman, and H. Atwater, "Are negative index materials achievable with surface plasmon waveguides? A case study of three plasmonic geometries", *Optics Express* 16, 19001 (2008)

Featured in Nature Materials 7, 925 (2008) "True Negative Refraction"

[7] K. Diest, M. Archer, J. Dionne, M. Czubakowski, and H. Atwater "Silver diffusion bonding and layer transfer of lithium niobate to silver", *Applied Physics Letters* 93, 092906 (2008)

[8] E. Verhagen, J. Dionne, K. Kuipers, H. Atwater, A. Polman, "Near field visualization of strongly confined surface plasmon polaritons in metal-insulator-metal waveguides", *Nano Letters* 8, 2925 (2008)

Awarded best paper at the Nano Meta conference in Tirol, Austria

[9] H. Lezec*, J. Dionne*, and H. Atwater, "Negative refraction at visible frequencies", *Science* 316, 430 (2007) (*equal-author contributors)

Featured in Nature 445, 346 (2007) "How to drive light round the wrong bend"

Featured in Scientific American, "Visible light bent the 'wrong' way" (March 22, 2007)

[10] J. Dionne, H. Lezec, and H. Atwater, "Highly confined photon transport in subwavelength metallic slot waveguides" *NanoLetters* 6, 1928 (2006)

Featured in Nature Materials 5, 765 (2006) "Light at the End of the Waveguide"

Awarded best paper at the second Surface Plasmon Photonics conference in Graz, Austria

[11] J. Dionne, L. Sweatlock, A. Polman, and H. Atwater "Plasmon slot waveguides: Towards chip-scale propagation with subwavelenth-scale localization" *Phys. Rev. B* 73, 035407 (2006)

Selected for the Virtual Journal of Nanoscience

[12] J. Dionne, L. Sweatlock, A. Polman, and H. Atwater "Planar metal plasmon waveguides: frequency-dependent dispersion, propagation, localization, and loss beyond the free electron model" *Phys. Rev. B* 72, 075405 (2005)

[13] H. Atwater, S. Maier, A. Polman, J. Dionne, and L. Sweatlock, "The new 'PN junction': Plasmonics enables photonic access to the nanoworld" *MRS Bulletin* 30 (2005)

[14] H. Atwater, J. Dionne, L. Sweatlock, "Subwavelength-scale plasmon waveguides." Book chapter in *Surface Plasmon Photonics* (pp. 87-104), M. L. Brongersma and P. G. Kik (Ed.), Dordrecht, NL: Springer

Synergistic Activities

- Chair, Materials Research Society Symposium, "Plasmonic Materials & Metamaterials," Spring 2010 and Spring 2012
- Academic advisor to 8 Stanford freshman and 2 upperclassmen
- Elementary and middle-school outreach aimed at solar-energy education through "Chemistry in the Classroom" and Career Day outreach

Budget

Professor Dionne will expend 7.5% effort on this LDRD project (5% academic year and 15% summer quarter). Salary and tuition support is also requested for a 60% graduate student (50% in the academic year, and 90% in the summer quarter). The graduate student will work on the modeling, synthesis, and characterization of high-frequency metamaterials. Funding requested for materials and supplies will cover the costs of chemical reagents, optical and electronic components, and software to complete the synthesis and optical characterization of our metamaterials, both experimentally and theoretically. Funds also are requested to cover the costs of using shared nanofabrication and characterization facilities, including an evaporator, scanning electron microscope, and transmission electron microscope. Additional funds will cover the cost of access to a shared SEM-based cathodo-luminescence setup, to detect the light emission from our meta-materials upon electron excitation. Partial funds will also be used to cover a shared, in-situ TEM holder with an optical fiber for optical excitation and/or detection in a TEM. Total estimated costs for year one are $149.9k, year 2 are $149.3k and year 3, $150.9k.

Approvals

Nancy Matlin

Nancy Matlin, Associate Director, Division of Materials Sciences

Zhixun Shen

ZX Shen, Director, Division of Materials Sciences

Keith Hodgson, Associate Laboratory Director, Photon Science Directorate