

Lights, nano, action! New plasmonic materials and methods to probe nanoscale phenomena

Jennifer A. Dionne

This article is based on a presentation given by Jennifer A. Dionne for the Kavli Early Career Lecture-ship in Nanoscience on December 1, 2013, at the 2013 Materials Research Society Fall Meeting in Boston.

The field of plasmonics has transformed the ability to control nanoscale light-matter interactions with applications ranging from high-efficiency photovoltaic modules to ultrasensitive biodetectors, electromagnetic cloaks, and subwavelength integrated photonic circuits. This article summarizes my group's efforts to contribute to this burgeoning field, with emphasis on our research in quantum plasmonics and optical-frequency magnetism. First, we explore the plasmon resonances of individual nanoparticles as they transition from a classical to a quantum-influenced regime. We then utilize these results to directly monitor hydrogen absorption and desorption in individual palladium nanocrystals. Subsequently, using real-time manipulation of plasmonic particles, we investigate plasmonic coupling between pairs of particles separated by nanometer- and angstrom-scale gaps. For sufficiently small separations, we observe the effects of quantum tunneling between particles on their plasmonic resonances. Finally, using the properties of coupled metallic nanoparticles, we demonstrate the colloidal synthesis of an isotropic metafluid or "metamaterial paint" that exhibits a strong optical-frequency magnetic response and the potential for negative permeabilities and negative refractive indices.

Introduction

In 1833, Faraday combined silver and sulfur and discovered the first material with a negative temperature coefficient of resistance, silver sulfide. At the time, the word semiconductor did not exist. Yet we now know that this first semiconducting material laid the foundation for an entirely new and extremely important class of electronic materials. Today, a similar revolution is unfolding for optical materials. Textbook conceptions of light-matter interactions, such as the notions of exclusively positive refractive indices¹⁻⁵ and reciprocal light propagation,⁶⁻¹² are being redefined by new optical materials. These materials allow light to be controlled in ways previously thought impossible, providing techniques to circumvent the diffraction limit of light and tune both electric and magnetic light-matter interactions.

At Stanford University, my research team is developing such new optical materials and using them to directly visualize, probe, and control nanoscale systems and phenomena—particularly

those relevant to energy and biology. We aim to address questions such as: Can optical microscopy achieve a resolution comparable to electron microscopy to study nanoscale systems *in situ* and in real time? Can catalytic processes be probed on the single particle or molecule level, to understand and improve catalytic reactions? Can proteins or small molecules be optically trapped and manipulated *in vivo* to directly probe molecular mechanics and interactions in cells? Though seemingly diverse, these questions all require precise control of light-matter interactions across wavelength and sub-wavelength scales, as enabled by new optical and plasmonic materials.

To tailor light-matter interactions, noble metal nanoparticles provide a particularly versatile platform. In this article, first we explore the impact of quantum effects on the plasmonic properties of small (<5 nm) noble metal nanoparticles.¹³ To correlate the spectral properties of particles with their structure, we utilize electron energy-loss spectroscopy (EELS) in

a transmission electron microscope (TEM). We then describe how plasmon-EELS can be used as a new, powerful method to monitor phase transitions of individual metallic particles using the hydrogenation of palladium as an example.¹⁴

Next, we discuss the plasmons of coupled nanoparticles. The electron beam in our TEM-EELS platform can be used to dynamically change the interparticle separation of particle pairs. For sufficiently close separations (<1 nm), electrons tunnel between the particles, significantly impacting the far-field optical response of plasmonic particle dimers.¹⁵

Finally, we transition from investigations of electric dipolar plasmon resonances to magnetic dipolar resonances. We describe our research efforts to create a liquid metamaterial or “meta-fluid” that exhibits a tunable magnetic permeability and the potential for a negative refractive index at optical frequencies.¹⁶ Our approach is based on protein-directed assembly of non-magnetic plasmonic metallic nanoparticles. Both individual nanoparticle clusters and the resulting bulk colloidal metamaterial respond strongly to the driving magnetic field of light, providing the foundation for future “gram-scale” metamaterial paints, which could be readily applied to any surface.

A primer on classical plasmon resonances

Consider illuminating a conducting particle, such as a metallic nanoparticle or a heavily doped semiconducting particle. Light consists of an alternating current (AC) electric field that drives the free electrons of the particle to oscillate. The collective oscillation of free electrons in response to a driving field is known as a plasmon. For a particle much smaller than the wavelength of light, the electron oscillation mimics an electric dipole, and the particle’s polarizability α can be written in terms of its radius r , its permittivity ϵ , and the permittivity of the surrounding medium, ϵ_s :

$$\alpha = 4\pi r^3 \frac{\epsilon - \epsilon_s}{\epsilon + 2\epsilon_s}. \quad (1)$$

Note that the denominator in this expression can approach zero, since ϵ for conducting materials is negative across certain frequencies. Therefore, the polarizability of conducting particles can be extraordinarily high, a result that directly impacts the scattering and absorption cross-sections of the particle. As an example, a silver nanoparticle embedded in vacuum ($\epsilon_s = 1$) will exhibit a peak in its polarizability when $\epsilon = -2$. The bulk permittivity of silver has a real component equal to -2 at a wavelength of 355 nm, which yields a peak in the absorption efficiency, and hence a plasmonic resonance at that same wavelength.

An important feature of plasmon resonances is their tunability with properties such as the geometry of the particle (i.e., size and shape), the refractive index of the surrounding medium, and the electron density or charge of the nanoparticle. Many applications of plasmon resonances have relied on this tunability, and a few are highlighted here to illustrate the breadth of the field.^{17,18}

First, plasmon particles have found extensive applications in medical imaging and therapeutics, including photoacoustic imaging, photothermal cancer treatments, and drug delivery.^{19,20} Second, plasmon resonances can be used to increase the efficiency of solar energy conversion (i.e., by increasing the absorption cross-section of photovoltaic materials or by preferentially scattering sunlight into the active layers of a photovoltaic cell).^{21,22} For example, plasmons have increased the efficiency of thin-film amorphous silicon cells from 4.8% to over 6%—a significant improvement in cell efficiency, simply by patterning the back contact of the cell to support surface plasmons.²³ Third, surface plasmons have been used to create optical tweezers that can directly trap and manipulate subwavelength particles and even proteins, giving new insights into protein folding and unfolding.^{24–26} Finally, because surface plasmons are sensitive to changes in refractive indices and charges, they can be used to sensitively detect molecular absorption, redox reactions, and catalysis.^{27–31}

Given the importance and broad applicability of particle plasmon resonances, two features are particularly surprising. First, most applications of plasmonic nanoparticles appear to rely on larger nanoparticles, with dimensions greater than 10 nm. That size may seem small, but we questioned what unusual effects might emerge if plasmons were to be confined to even smaller spaces, where quantum effects such as energy discretization and tunneling may play an important role. Second, most applications of plasmonic particles rely on electric resonances (i.e., how the electric field of light drives the electrons in the nanoparticle). How might their optical response change if they could also respond to the magnetic field of light? The field of metamaterials provides a solid roadmap for the intriguing properties accessible with magnetic resonances, including negative and near-zero refractive indices—essentially, tunable refractive indices beyond the library of naturally occurring materials. To my knowledge, there was no demonstration of a colloidal metamaterial that could form the basis for metamaterial liquids or paints. These two questions drove my initial research in this field.

Quantum-influenced plasmon resonances of individual particles

Nearly five decades of elegant experiments have aimed to unravel the intrinsic plasmonic properties of very small particles; however, these measurements have contended with several significant challenges. To begin with, very small sub-10-nm particles are characterized by extremely weak optical scattering, with particle absorption dominating over scattering. To overcome this weak scattering, typical experiments measure the plasmon resonances of ensembles of particles. Such measurements suffer from the effects of particle heterogeneity, meaning no techniques can produce particles that are all identical in size, shape, and aspect ratio, and, accordingly, any ensemble measurement will result in broader spectral line shapes than would

be characteristic of a truly monodisperse sample. Further, as implied by Equation 1, larger particles in the ensemble will dominate the plasmonic response even if they constitute a small fraction of particles in the ensemble. Finally, ligands add yet another complicating factor to the interpretation of the plasmonic spectra. Since plasmons are sensitive to the refractive index of the surrounding medium, the surface functionalization of the particle can influence the spectra. Importantly, the smaller the particle, the larger the impact of the ligands.

Inspired by prior measurements on small plasmonic particles,^{32–34} our approach utilized single-particle techniques that enabled correlation of particle spectra with particle structure. We used monochromated EELS in a TEM to achieve both atomic-scale spatial resolution and very high spectral resolution.¹³ The concept is outlined in **Figure 1**. An electron beam is focused to a spot size of roughly 0.25 nanometers and then passed through a sample of nanoparticles on an electron transparent substrate. Upon interaction with a nanoparticle, the electron beam excites the various modes of the particle, including the surface plasmon resonance and the bulk plasmon resonance. The electron beam therefore loses energy corresponding to the energy of these modes, and the detector measures this energy loss. Importantly, various resonances of the particle can be selectively excited based on the electron beam position. For example, for a subwavelength spherical particle, a beam position near the edge of the particle excites the surface plasmon resonance, while a beam position near the center of the particle excites the bulk plasmon resonance.

TEM-EELS has seen significant advances in the last few years, and an imaging resolution of 0.07 nm is now achievable. To illustrate the extraordinary imaging capabilities of this system, Figure 1b includes electron micrographs of synthesized silver nanoparticles. Our synthesis yielded particles with sizes ranging from 20 nm to about 1 nm. Further, to circumvent the effects of ligands that might otherwise shift or dampen the surface plasmon resonances, our particles were synthesized without organic ligands.¹³

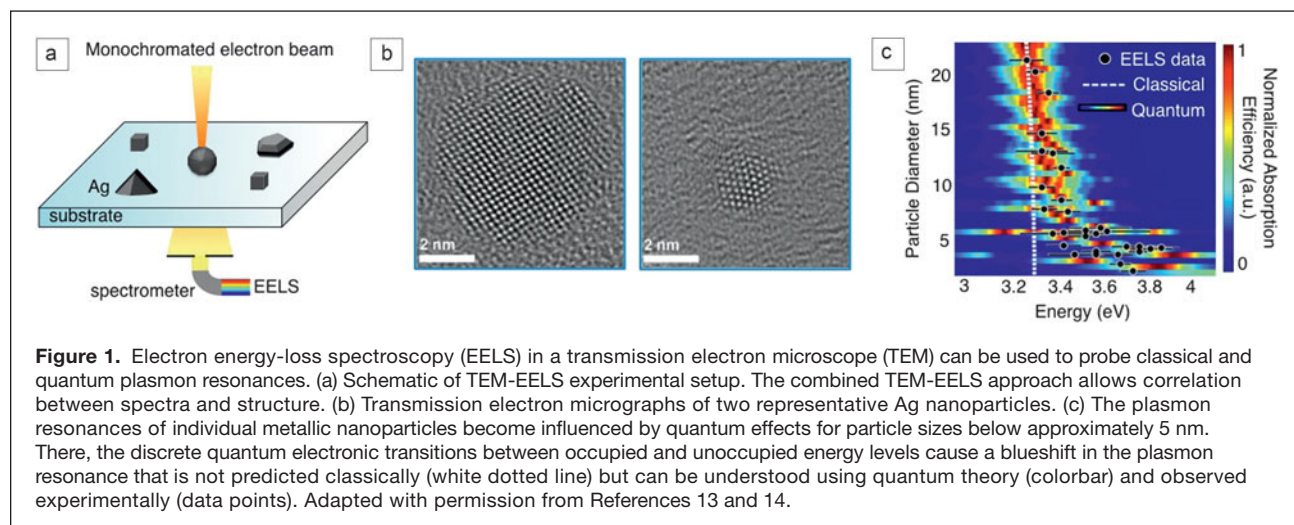
What happens to plasmon resonances as the particle size is reduced? Our experiments revealed two significant trends. First, we noticed a significant, ~ 0.5 eV, blueshift of the peak resonance energy, illustrated in Figure 1c. As seen in the experimental EELS data, the blueshift is especially pronounced for particles smaller than 5 nm in diameter. Additionally, the spectral linewidth increased, corresponding to a reduced plasmon lifetime.

How might we explain the significant blueshift and linewidth broadening? One approach considers the increased scattering frequency of electrons as the particle size is reduced. This approach accounts for the observed peak broadening, but actually predicts a slight redshift for noble metal plasmon resonances. Instead, we considered a quantum approach, which models the impact of discrete electronic transitions on the surface plasmon resonance. The calculated spectra for various particle sizes are shown in Figure 1c (the color map corresponds to the absorption efficiency, analogous to the electron energy-loss probability). Our experimental data agree and are in striking contrast to what a purely classical model would predict (white dotted line).

These results suggest two somewhat unexpected conclusions. First even though our particles consist of hundreds of atoms, the discretization of energy levels still impacts the plasmon resonance. Second, even though our particles are significantly larger than the de Broglie wavelength of an individual electron, collective oscillations of electrons (i.e., plasmons) experience quantum confinement.

Monitoring catalytic reactions on single particles

Smaller plasmonic particles tend to make excellent sensors, owing to their large surface-area-to-volume ratio. They also tend to make better catalysts. For example, the catalytic activity for CO oxidation on gold nanoparticles is negligible for particles above 5 nm in size but increases exponentially for smaller sizes.³⁵ Additionally, many open



questions remain about the nature of phase transitions in small particles. This intercalation-driven phase transition presents a simple model system to explore the thermodynamics relevant to many energy and information processes, including hydrogen storage, battery charging, and memory switching. As seen in **Figure 2a**, palladium hydride undergoes a transition from a dilute α phase to a hydrogen-rich, lattice-expanded β phase with increasing hydrogen gas pressure. Recent studies of nanoscale palladium hydride systems have revealed significant thermodynamic deviations from the bulk.³⁶ For example, ensemble measurements of Pd nanocrystals as large as 65 nm have suggested sloped pressure–composition isotherms,³⁷ in striking contrast to the sharp α to β phase transitions observed in bulk palladium. To identify whether such results are intrinsic to the nanoparticles or arise from heterogeneity in the sample, single-particle measurements are essential.

Inspired by single-particle work utilizing plasmonic nanoantennas,^{38,39} we sensed the α to β phase transition utilizing

in situ, environmental TEM-EELS.¹⁴ The phase change of individual palladium nanocrystals was monitored by probing their bulk plasmon resonance—a direct measure of the material phase and composition. Importantly, this technique is more sensitive than prior techniques and allows ready correlation between particle structure and spectra.

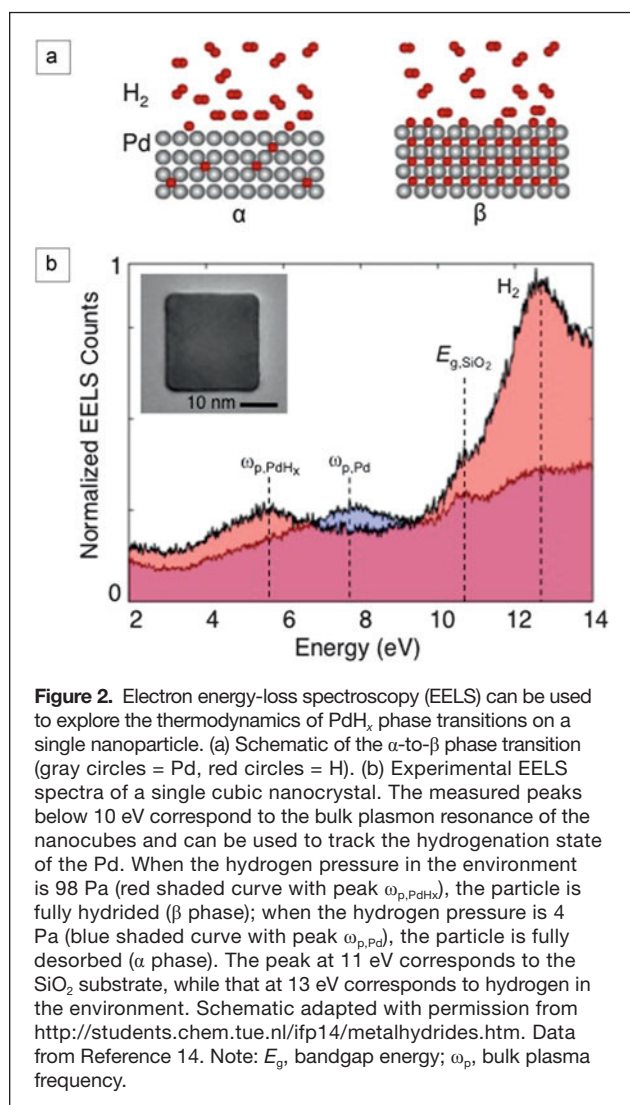
Figure 2b illustrates example experimental EELS spectra on a single Pd nanocube, acquired at two different H₂ pressures: $P = 4$ Pa (blue shaded region) and $P = 98$ Pa (after hydrogen absorption, red shaded curve). The measured peaks below 10 eV correspond to the bulk plasmon resonance of the nanocrystal and can be used to track the hydrogenation state of the Pd. Upon increasing the hydrogen pressure, a large and reversible shift in the plasmon resonance marks the transition from the α phase (peak at 7.7 eV) to the β phase (peak at 5.6 eV). Peaks at 11 eV and 13 eV correspond to the SiO₂ substrate and the presence of hydrogen in the environment, respectively, and merely change their amplitude with increasing/decreasing hydrogen pressure.

Our ongoing work in this area is aimed at constructing full pressure–composition isotherms on a variety of nanocrystal sizes and shapes. Experiments to date indicate several intriguing trends for the thermodynamic properties of nanocubes, including abrupt transitions between the α and β phases for particles larger than 15 nm and size-dependent loading pressures, with larger particles tending to load at higher equilibrium pressures.¹⁴ It is our hope that this environmental TEM-EELS approach will provide a new high-resolution technique for unraveling unknown or unresolved thermodynamic processes on individual particles.

Quantum-influenced plasmon resonances: coupled particles

Coupled plasmonic particles can be used as sensitive surface-enhanced Raman spectroscopy platforms, molecular rulers, and novel nanoantennas.^{40–42} Numerous studies have elegantly explored the dependence of plasmon resonances on interparticle separation.^{43–47} But what happens when particles get so close that electrons can tunnel between particles? In 2009, Nordlander and colleagues showed theoretically that quantum tunneling between two plasmonic nanoparticles reduces the electric field intensity in the particle junction and causes a relative blueshift of the dimer plasmon resonance, compared with classical predictions.⁴⁸ These effects could impact the design of future quantum plasmonic nanoantennas and molecular sensors; they could also enable entirely new quantum plasmonic devices and novel molecular optoelectronic applications. However, observing the effects of quantum tunneling would require interparticle separations approaching 0.5 nm—a challenging feat for most traditional fabrication methods.

To explore the plasmonic properties of coupled particles in the quantum-tunneling regime, we again relied on TEM-EELS.¹⁵ Somewhat fortuitously, we discovered that



ligand-free nanoparticles were mobile under appropriate electron beam conditions. As we focused the electron beam to a small probe size, we could move 10 nm diameter nanoparticles at a rate of about 0.02 nm per second—allowing one particle to approach another with high precision. Concurrently, we could use EELS to map the plasmonic modes of the dimer.

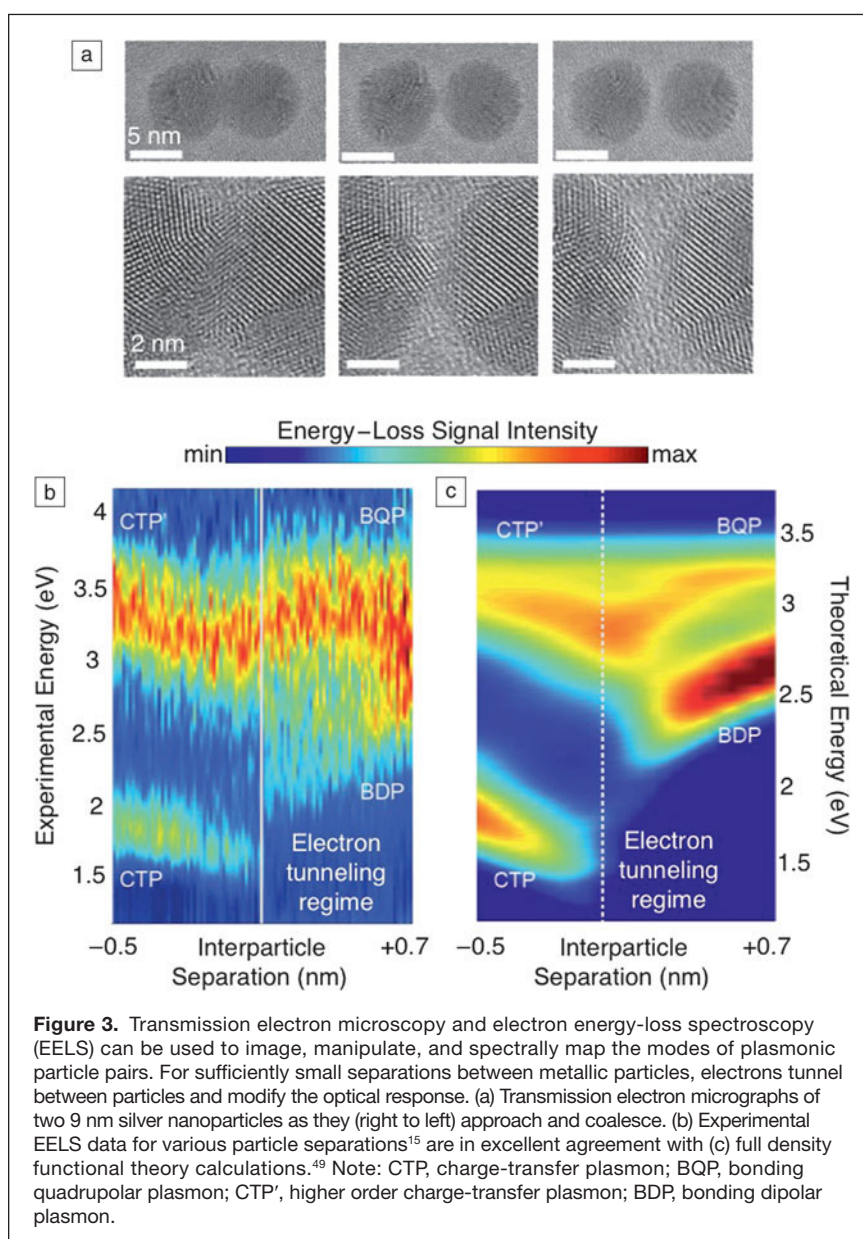
Figure 3a includes transmission electron micrographs of two 9 nm silver nanoparticles as they approach and coalesce. For particles separated by a 1 nm gap, EELS resolves the particle's bonding dipolar and quadrupolar resonances. Once the particles merge, a very low energy mode appears, corresponding to a charge-transfer mode. Such modes could be readily understood using classical electromagnetism. However, some intriguing trends were observed for interparticle separations in the sub-nanometer regime, as highlighted in **Figure 3b**. This figure plots experimental EELS spectra for particles with separations ranging from approximately +0.7 nm to -0.5 nm. Here, a positive separation means that the particles are separated by a gap, while a negative separation means that the particles are overlapping. For separations less than about 0.7 nm, the bonding dipolar plasmon significantly decreases in intensity and exhibits a slight redshift. Classical predictions, which assume that electrons are confined to the particle by an infinite potential well, would have predicted a stronger bonding dipolar plasmon as well as a significant redshift to extremely low energies. Our experiment only matches these classical experiments for separations exceeding ~1 nm.

To explain our results, we again turned to quantum theory.⁴⁸⁻⁵⁰ We know that electrons are not confined to an infinite potential well. Instead, they are confined by a finite potential well that is determined by the work function of the metal. In the presence of an applied electric field, the electrons can tunnel over this work function into the neighboring particle. This tunneling will significantly impact plasmonic properties. In the case of nearly touching particles, the electron current in the gap will dampen the bonding dipolar plasmon and cause a relative blueshift; further, for just-overlapping particles, quantum effects will also dampen the charge-transfer plasmon. Javier Aizpurua has performed density functional theory calculations to account for these quantum effects in plasmon particle pairs.⁴⁹ The results are included in **Figure 3c** and show remarkable agreement with our experimental results. Most surprising about these results is that quantum effects can significantly impact the far-field optical properties of classically

sized particles. Additionally, the direct observation of quantum tunneling implies that *in situ* assembly and analysis of new quantum plasmonic materials and devices is possible.

A metafluid exhibiting strong visible frequency magnetism

Our discussion has concentrated on the electric resonances of particles, which result from the interaction of AC electric fields with a particle's free electrons. Are magnetic resonances, which result from interaction of AC magnetic fields with particles, possible? Indeed they are. While most materials are "blind" to the magnetic field of light, the field of metamaterials has enabled some remarkably exciting materials exhibiting optical-frequency magnetism. For example, engineered metamaterials with a tunable electric permittivity and magnetic permeability



can exhibit refractive indices different from the library afforded by naturally occurring materials, such as negative and near-zero refractive indices.^{1–5} Additionally, metamaterials and metasurfaces exhibiting optical magnetism can enhance the efficiency of natural magnetic or mixed electric–magnetic transitions.^{51,52} Such effects can be used to enable new, more sensitive chiral spectroscopies or even enantioselective syntheses (i.e., syntheses that favor formation of a specific enantiomer).⁵³

Planar multiparticle assemblies (such as a plasmonic trimer or asymmetric dimer) support optical frequency magnetic modes but only for a particular angle of incidence and for a particular polarization.^{54–56} Inspired by several theoretical studies,^{57–59} we wondered if we could create a metamaterial exhibiting optical magnetism for all illumination angles and polarizations. Further, we sought to create such materials using colloidal synthesis to yield a metafluid. Such a metamaterial liquid or gel would combine the advantages of solution-based processing with facile integration into conventional optical components or networks. For example, a negative or near-zero index fluid could be coated onto existing imaging arrays to enhance the detection resolution. Alternatively, the metamaterial solution could be sprayed onto the surface of microelectromechanical devices to prevent stiction or on the surface of bulk devices to control scattering and absorption.

Our approach relied on protein-directed assembly of plasmonic nanoparticles in aqueous solution.¹⁶ Silver nanoparticles functionalized with biotin were mixed with silica nanoparticles functionalized with the protein streptavidin. Based upon the strong biotin–streptavidin interactions, the silver nanoparticles formed concentric loops around silica cores (see **Figure 4a**); the initial and resulting colloidal solutions are shown in **Figure 4b**. High resolution transmission electron microscopy and scanning electron microscopy confirmed the three-dimensional nature of the assembled metamolecules. Both single-particle spectroscopy and ensemble measurements confirmed the magnetic response. At a wavelength of 630 nm, magnetic dipole scattering from the bulk solution was measured to be 12% of the strength of the

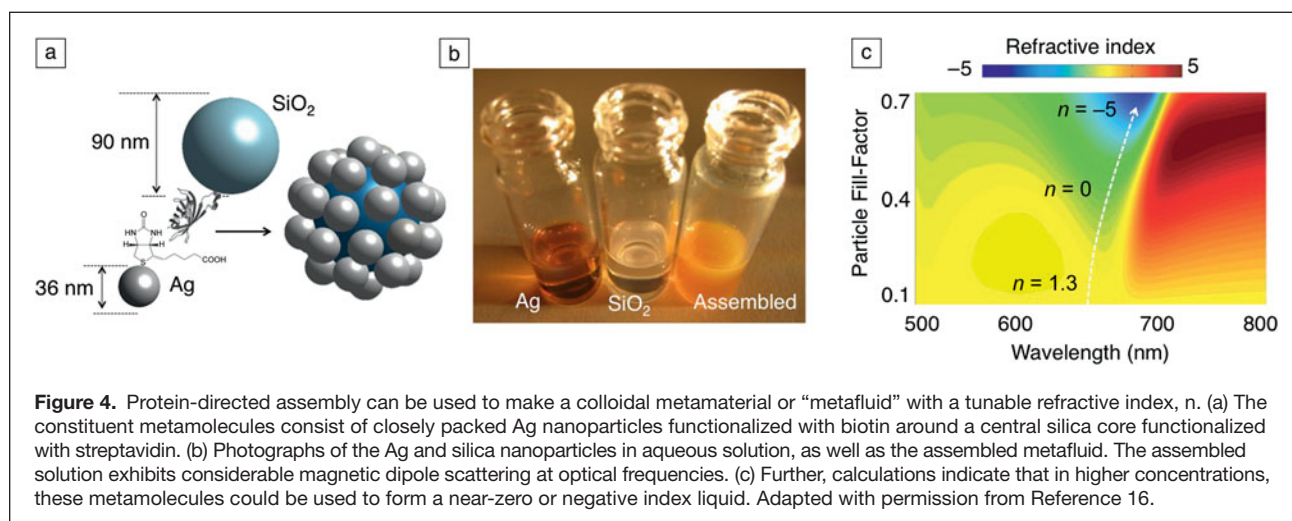
electric dipole—significant for a bulk nanoscale system at optical frequencies. This magnetic response could in turn be used to create a tunable index fluid. For example, **Figure 4c** plots calculations of the effective refractive index of the solution as a function of metamolecule concentration. For particle packing fractions (i.e., fill factors) exceeding 40%, the resulting metamaterial can exhibit effective refractive indices below zero. While we have yet to achieve such high yields, our colloidal approach may ultimately enable metamaterial synthesis on gram or kilogram-scales, accelerating development of advanced metamaterial- and/or metasurface-based devices.

Outlook

Plasmonic materials and metamaterials have opened up profound ways to control light–matter interactions across wavelength and sub-wavelength scales. Advances in these materials are poised to impact fields ranging from catalysis to computing, solar energy, microscopy, and molecular electronics. Our work on quantum plasmonics and optical-frequency magnetism is but a small contribution to the nanophotonics community, but one that we hope will incite new questions and perhaps new research directions. As Faraday said, “It is the great beauty of our science ... that advancement in it, whether in a degree great or small, instead of exhausting the subjects of research, opens the doors to further and more abundant knowledge, overflowing with beauty and utility.”⁶⁰

Acknowledgments

I gratefully acknowledge the Kavli Foundation, the Materials Research Society, and my nominators who believed in the promise of my research. Enormous gratitude goes to my group at Stanford University, who through hard work, dedication, and occasional perspiration, helped make my scientific vision a reality. I especially thank those students and postdocs whose work was featured in this article: Jonathan Scholl, Aitzol Garcia-Etxarri, Ashwin Atre, Andrea Baldi, Tarun Narayan, Sassan Sheikholeslami, and Hadiseh Alaieian of Stanford



University. I also acknowledge my collaborators Ai Leen Koh and Albert Polman, whose support and insights have proven invaluable. Our work is made possible by the generous support of funding agencies, including the Air Force Office of Scientific Research (FA9550-15-1-0006 and FA9550-11-1-0024), the National Science Foundation (DMR-1151231), the Department of Energy (DE-EE0005331), and the Global Climate and Energy Project at Stanford.

References

1. J. Valentine, S. Zhang, T. Zentgraf, E. Ulin-Avila, D.A. Genov, G. Bartal, X. Zhang, *Nature* **455**, 376 (2008).
2. H.J. Lezec, J.A. Dionne, H.A. Atwater, *Science* **316**, 430 (2007).
3. C.M. Soukoulis, M. Wegener, *Nat. Photonics* **5**, 523 (2011).
4. V. Shalaev, *Nat. Photonics* **1**, 1 (2007).
5. N. Yu, F. Capasso, *Nat. Mater.* **13**, 139 (2014).
6. B. Peng, Ş.K. Özdemir, F. Lei, F. Monifi, M. Gianfreda, G.L. Long, S. Fan, F. Nori, C.M. Bender, L. Yang, *Nat. Phys.* **10**, 394 (2014).
7. A. Guo, G.J. Salamo, D. Duchesne, R. Morandotti, M. Volatier-Ravat, V. Aimez, G.A. Siviloglou, D.N. Christodoulides, *Phys. Rev. Lett.* **103**, 093902 (2009).
8. L. Feng, *Nat. Mater.* **12**, 108 (2012).
9. C.E. Rüter, K.G. Makris, R. El-Ganainy, D.N. Christodoulides, M. Segev, D. Kip, *Nat. Phys.* **6**, 192 (2010).
10. N. Lazarides, G. Tsironis, *Phys. Rev. Lett.* **110**, 053901 (2013).
11. L. Chang, X. Jiang, S. Hua, C. Yang, J. Wen, L. Jiang, G. Li, G. Wang, M. Xiao, *Nat. Photonics* **8**, 524 (2014).
12. S. Longhi, *Phys. Rev. A* **82**, 031801 (2010).
13. J.A. Scholl, A.L. Koh, J.A. Dionne, *Nature* **483**, 421 (2013).
14. A. Baldi, T.C. Narayan, A.L. Koh, J.A. Dionne, *Nat. Mater.* **13**, 1143–1148 (2014).
15. J.A. Scholl, A. García-Etxarri, A.L. Koh, J.A. Dionne, *Nano Lett.* **13**, 564 (2013).
16. S.N. Sheikholeslami, H. Alaeian, A.L. Koh, J.A. Dionne, *Nano Lett.* **13**, 4137 (2013).
17. Y. Xia, N. Halas, *MRS Bull.* **30**, 338 (2005).
18. J.A. Dionne, H.A. Atwater, *MRS Bull.* **37**, 717 (2012).
19. Y. Xia, W. Li, C.M. Cobley, J. Chen, X. Xia, Q. Zhang, M. Yang, E.C. Cho, P.K. Brown, *Acc. Chem. Res.* **44**, 914 (2011).
20. R. Bardhan, S. Lal, A. Joshi, N.J. Halas, *Acc. Chem. Res.* **44**, 936 (2011).
21. H.A. Atwater, A. Polman, *Nat. Mater.* **9**, 205 (2010).
22. K.R. Catchpole, A. Polman, *Opt. Express* **16**, 21793 (2008).
23. V.E. Ferry, M.A. Verschuuren, H.B.T. Li, R.E.I. Schropp, H.A. Atwater, A. Polman, *Appl. Phys. Lett.* **95**, 183503 (2009).
24. M.L. Juan, M. Righini, R. Quidant, *Nat. Photonics* **5**, 349 (2011).
25. A. Zehetabi-Oskuie, H. Jiang, B.R. Cyr, D.W. Rennehan, A.A. Al-Balushi, R. Gordon, *Lab Chip* **13**, 2563 (2013).
26. A.A.E. Saleh, J.A. Dionne, *Nano Lett.* **12**, 5581 (2012).
27. K.A. Willets, R.P. Van Duyne, *Annu. Rev. Phys. Chem.* **58**, 267 (2007).
28. K.M. Mayer, J.H. Hafner, *Chem. Rev.* **111**, 3828 (2011).
29. K.-S. Lee, M.A. El-Sayed, *J. Phys. Chem. B* **110**, 19220 (2006).
30. C. Novo, A.M. Funston, P. Mulvaney, *Nat. Nanotechnol.* **3**, 598 (2008).
31. M.L. Tang, N. Liu, J.A. Dionne, A.P. Alivisatos, *J. Am. Chem. Soc.* **133**, 13220 (2011).
32. S. Peng, J.M. McMahon, G.C. Schatz, S.K. Gray, Y. Sun, *Proc. Natl. Acad. Sci. U.S.A.* **103**, 14530 (2010).
33. K. Lindfors, T. Kalkbrenner, P. Stoller, V. Sandoghdar, *Phys. Rev. Lett.* **93**, 037401 (2004).
34. S. Palomba, L. Novotny, R.E. Palmer, *Opt. Commun.* **281**, 480 (2008).
35. H. Falsig, B. Hvolbæk, I.S. Kristensen, T. Jiang, T. Bligaard, C.H. Christensen, J.K. Nørskov, *Angew. Chem.* **120**, 4913 (2008).
36. M. Yamauchi, R. Ikeda, H. Kitagawa, M. Takata, *J. Phys. Chem. C* **112**, 3294 (2008).
37. R. Bardhan, L.O. Hedges, C.L. Pint, A. Javey, S. Whitlam, J.J. Urban, *Nat. Mater.* **12**, 905 (2013).
38. T. Shegai, C. Langhammer, *Adv. Mater.* **23**, 4409 (2011).
39. N. Liu, M. Lee Tang, M. Hentschel, H. Giessen, A.P. Alivisatos, *Nat. Mater.* **10**, 631 (2011).
40. W. Zhang, L. Huang, C. Santschi, O.J.F. Martin, *Nano Lett.* **10**, 1006 (2010).
41. C.E. Talley, J.B. Jackson, C. Oubre, N.K. Grady, C.W. Hollars, S.M. Lane, T.R. Huser, P. Nordlander, N.J. Halas, *Nano Lett.* **5**, 1569 (2005).
42. C. Sönnichsen, B.M. Reinhard, J. Liphardt, A.P. Alivisatos, *Nat. Biotechnol.* **23**, 741 (2005).
43. H. Duan, A.I. Fernández-Domínguez, M. Bosman, S.A. Maier, J.K.W. Yang, *Nano Lett.* **12**, 1683 (2012).
44. P.K. Jain, M.A. El-Sayed, *Chem. Phys. Lett.* **487**, 153 (2010).
45. J. Merlein, M. Kahl, A. Zuschlag, A. Sell, A. Halm, J. Boneberg, P. Leiderer, A. Leitenstorfer, R. Bratschitsch, *Nat. Photonics* **2**, 230 (2008).
46. L. Yang, H. Wang, B. Yan, B.M. Reinhard, *J. Phys. Chem. C* **114**, 4901 (2010).
47. C. Ciraci, R.T. Hill, J.J. Mock, Y. Urzhumov, A.I. Fernández-Domínguez, S.A. Maier, J.B. Pendry, A. Chilkoti, D.R. Smith *Science* **337**, 1072 (2012).
48. J. Zuloaga, E. Prodan, P. Nordlander, *Nano Lett.* **9**, 887 (2009).
49. R. Esteban, A.G. Borisov, P. Nordlander, J. Aizpurua, *Nat. Commun.* **3**, 825 (2012).
50. D.C. Marinica, A.K. Kazansky, P. Nordlander, J. Aizpurua, A.G. Borisov, *Nano Lett.* **12**, 1333 (2012).
51. N. Noginova, G. Zhu, M. Mavy, M.A. Noginov, *J. Appl. Phys.* **103**, 07E901 (2008).
52. J. Schuller, R. Zia, T. Taubner, M. Brongersma, *Phys. Rev. Lett.* **99**, 107401 (2007).
53. A. García-Etxarri, J.A. Dionne, *Phys. Rev. B: Condens. Matter* **87**, 235409 (2013).
54. J.A. Fan, C. Wu, K. Bao, J. Bao, R. Bardhan, N.J. Halas, V.N. Manoharan, P. Nordlander, G. Shvets, F. Capasso, *Science* **328**, 1135 (2010).
55. F. Shafiei, F. Monticone, K.Q. Le, X.-X. Liu, T. Hartsfield, A. Alù, X. Li, *Nat. Nanotechnol.* **8**, 95 (2013).
56. S.N. Sheikholeslami, A. García-Etxarri, J.A. Dionne, *Nano Lett.* **11**, 3927 (2011).
57. Y.A. Urzhumov, G. Shvets, J. Fan, F. Capasso, D. Brandl, P. Nordlander, *Opt. Express* **15**, 1 (2007).
58. A. Alu, A. Salandrino, N. Engheta, *Opt. Express* **14**, 1 (2006).
59. A. Vallechi, M. Albani, F. Capolino, *Opt. Express* **19**, 1 (2011).
60. M. Faraday, *Experimental Researches in Electricity*, vol. 2, p. 257 (1834). □



Jennifer A. Dionne is an assistant professor in the Department of Materials Science and Engineering at Stanford University. She received BS degrees in physics and electrical and systems engineering from Washington University in St. Louis, Mo., in 2003, and her PhD degree in applied physics from the California Institute of Technology in 2009, under the supervision of Harry Atwater. She joined Stanford University in 2010 following a postdoctoral research fellowship at the University of California–Berkeley, and Lawrence Berkeley National Laboratory, working with Paul Alivisatos. Dionne's research develops new optical materials for applications

ranging from high-efficiency solar energy conversion to bioimaging and manipulation. Her work has been recognized with a Presidential Early Career Award in Science and Engineering, NSF CAREER Award, AFOSR Young Investigator Award, Outstanding Young Alum Award from Washington University in St. Louis, Hellman Fellowship, and the Materials Research Society Graduate Student Gold Award. In 2011, Dionne was named one of *MIT Technology Review's* TR35-35 international innovators under 35 tackling important problems in transformative ways. Dionne can be contacted by email at jdionne@stanford.edu.



GET SOCIAL AT www.mrs.org/social-media



New from the
ADVANCED MATERIALS journal family

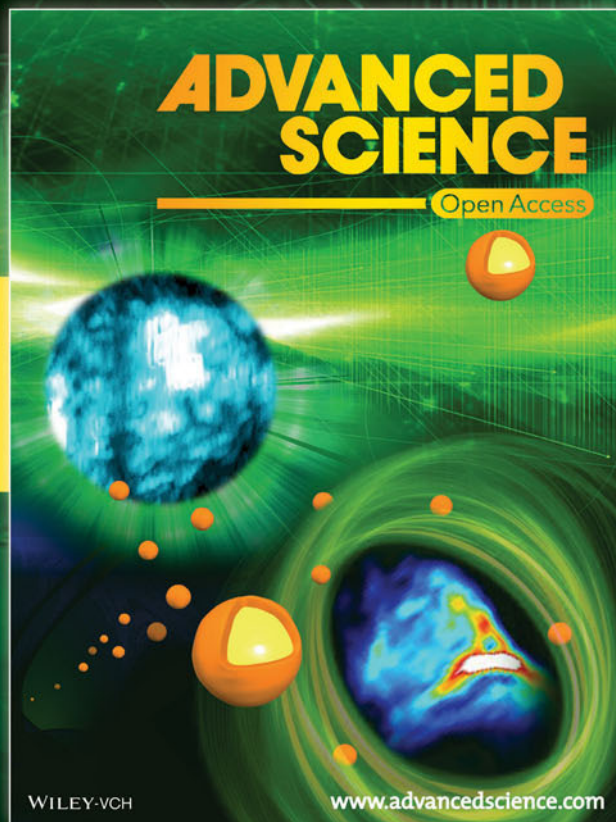
ADVANCED SCIENCE

Open Access

Premium open access
journal publishing research
from all areas of science

Submit your work now:
[www.editorialmanager.com/
advancedscience](http://www.editorialmanager.com/advancedscience)

- Fast, rigorous peer-review
- Highest quality research
- Covers all areas of science
- Rapid publication of accepted articles
- Freely available on Wiley Online Library and PubMed Central
- Authors retain copyright
- Articles published with Creative Commons Attribution (CC-BY) licenses



WILEY-VCH

www.advancedscience.com

WILEY

Materials Research Society®

University Chapters

The Materials Research Society® (MRS) University Chapter Program is a passionate and talented network of students from universities around the world. Supported by the Materials Research Society Foundation, the program fosters an environment for collaboration and open exchange of ideas across all scientific disciplines, spanning campuses and continents. These students represent the next generation of materials research and are preparing to carry the torch forward, advancing materials and improving the quality of life.

You'll find starting an MRS University Chapter is a fun and exceptionally valuable experience. Working through your Chapter—hosting events, creating special projects and connecting with experts from around the world—will prepare you for future professional and leadership roles in the materials community. Your Chapter can also play a vital role in bringing science to a broader audience. Now more than ever, the goal is to successfully bring research out of the laboratory and into the classroom and to the general public ... to show how materials have changed our history and continue to shape our future.

MRS continues to explore new ways to effectively foster growth of virtual global materials communities, using emerging technologies that are smart, fresh and innovative ... and that includes our University Chapters. With social media, MRS OnDemand® and two-way live streaming, we're already tapping into today's technologies to engage Chapters unable to attend our Meetings, but with the promise of new innovations, tools and devices, we continue to look ahead. **Help us build the Chapter of the Future!** Together we can design and develop virtual events to better collaborate, educate, participate and fascinate—across Chapters, across disciplines, across borders.

Now's the time to use your excitement, expertise and unique scientific perspectives to forge a new path. Join this international student community.

Start an MRS University Chapter today!



HELP US BUILD THE FUTURE

An International Community

One of the main objectives as graduate students and future researchers is to acquire the ability to build scientific networks for enhancing our vision, mission and scientific cooperation. MRS offers multiple tools to accomplish this with annual meetings, workshops, the MRS Bulletin and useful applications such as career connections or MRS OnDemand. Our MRS Student Chapter allowed us to obtain support from the Sociedad Mexicana de Materiales (SMM) that expands our national network. The formation of MRS Cinvestav Student Chapter not only allows us to integrate and exchange ideas as materials science students at Cinvestav, but also have the opportunity to know the science beyond our borders.

Natalia Tapia, Chapter President
Centro de Investigación y de Estudios Avanzados
del Instituto Politécnico Nacional (Cinvestav-IPN)
Mexico City, MEXICO

Interdisciplinary Collaboration

The MRS Student Chapter at WSU was organized by students who recognized the need to bring together a diverse group of students who were working in materials science. The campus is spread out geographically and students pursuing PhD degrees in MSE can be advised by chemistry or physics professors who are located far from the MSE department located in the engineering buildings. There is no distinction made between students whose advisors are in different departments or colleges, and the MRS Student Chapter has been a great vehicle to promote unity within the disciplines here.

David Field, Chapter Faculty Advisor
Washington State University
Pullman, Washington, USA

The MRS University Chapter Experience

The MRS University Chapter Program provides invaluable experiences and benefits for student members, but don't take our word for it. **Our Chapter Members Say It Best!**

Leadership Development

The Materials Research Society, along with our local Binghamton University Chapter, has positively influenced my commitment to materials science and technology. We were inspired by our advisor, Professor M. Stanley Whittingham, to start this Chapter ... and motivated by his enthusiasm and our faith to bring science to the general public, we continue to hold numerous events taken from MRS, i.e. MAKING STUFF and NanoDays. As our organization grows, we keep growing our events, and have found a solid and welcoming place in our community. Apart from the target audience, our events also benefit the volunteers, who gained valuable experience both from preparation, interaction, and activities. We feel proud and grateful to be part of an MRS University Chapter.

Tianchan Jiang, Chapter President
Binghamton University
Binghamton, New York, USA

Education Outreach

Our Chapter has enabled us to establish collaborations among the scientists on campus through informal social events, in addition to providing opportunities to participate in outreach. Integrating the science outreach efforts of Vanderbilt's community into our local community is one of our primary goals. As a University Chapter, we received a grant through the Materials Research Society Foundation to bring emerging materials science and hands-on activities to disadvantaged students and teachers in rural Tennessee. Without these seed funds, our Vanderbilt program, Materials Outreach for Rural Education (MORE), would not have been possible.

Amy Ng, Chapter President
Vanderbilt/Fisk Universities
Nashville, Tennessee, USA

Professional Growth

Starting and advising an MRS University Chapter is truly a rewarding experience. One can see professional growth of students, who start feeling like members of the worldwide materials research community. I come to MRS meetings with a "team," not just a couple of my students. Exciting initiatives and project ideas generated by students are amazing. Not surprisingly, some of the most prominent materials scientists, such as Millie Dresselhaus (MIT) or Stan Whittingham (SUNY Binghamton), have been acting as Faculty Advisors for many years.

Yury Gogotsi, Chapter Faculty Advisor
Drexel University
Philadelphia, Pennsylvania, USA

Building Chapters of the Future

I had the chance to present at the 2012 MRS Fall Meeting's Sustainability Forum, while being over 9000 km away from the meeting venue. I felt as if I was actually in Boston, being able to take questions, address them and getting into discussions with the committee. Thanks to the Materials Research Society and our local MRS-KAUST University Chapter for making this possible.

Ahmed E. Mansour, Chapter Vice President
King Abdullah University of Science and Technology (KAUST)
Thuwal, SAUDI ARABIA

Chapter Support

As a graduate student, it is key to broaden your spectrum of what is taking place in the research world in real time. MRS opens up many avenues, especially when working from a University Chapter. Direct contact with MRS associates helps keep everyone abreast of conferences, Chapter opportunities and activities that otherwise may not have been as easily accessible. MRS also rewards student memberships with rebates and travel expenditures, helping promote student involvement as well as Chapter building. We were able to host a multitude of meetings and seminars as well as send students to attend MRS conferences to promote their research.

Chinedu Okoro, Chapter President
Tuskegee University
Tuskegee, Alabama, USA

FOR MORE INFORMATION

on the MRS University Chapter Program,
visit www.mrs.org/university-chapters