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Foundations of Nanoscale Energy Transfer in Molecular Plasmonics

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Foundations of Nanoscale Energy Transfer in Molecular Plasmonics

Abstract. The objectives of the research program were centered around the common them of understanding plasmon-mediated and/or controlled energy transfer at the nanoscale. We examined the hypothesis that molecular-based models can be implemented to understand the mechanisms of how plasmonic nanoparticle networks transfer electromagnetic energy, and to determine what nanoparticle structures are most efficient for these applications. The research proceeded through five inter-related themes: 1) super-resolution nanostructure imaging using spatial localization of plasmon-mediated nonlinear optical (NLO) signals; 2) selective-amplification of light polarization states using asymmetric and chiral nanostructures; 3) quantification of plasmon-mode specific electronic coherence times; 4) development of ultrafast two-dimensional electronic spectroscopy for measuring strong inter-particle plasmon coupling; and 5) computational modeling of plasmon dynamics. Taken together, these thrusts provided insight into how the relative arrangement of metal nanostructures in a network determines the optical amplification and polarization selectivity of plasmonic networks. These structure-dependent properties are critical for determining material performance as functional components in light-harvesting applications such as solar-to-electric energy conversion, nonlinear optical limiting technology, ultrafast optical switching, analyte sensing, and quantum-state-specific excitation, among others. These new insights were obtained through advances in nonlinear optical imaging made in the Knappenberger lab, which include time-resolved (few femtosecond) and 3-D spatially resolved (approximately 1 nm latitudinal and 10 nm axial spatial accuracy) imaging measurements with single-particle sensitivity, and expansion of the computational capabilities of the Aikens group. The research activities advanced through strong synergistic collaboration between Prof. Ken Knappenberger (Florida State University), Christine Aikens
(Kansas State University), and Dr. Richard Vaia (AFRL).

Major Outcomes:

1. Super-resolution nanostructure imaging using spatial localization of plasmon-mediated nonlinear optical signals.

The primary objective of this research thrust was to understand how the relative orientations of plasmonic nanoparticles in a multi-particle network influenced the spatial localization of electromagnetic energy to specific regions within the assembly. Using an organized array of three spherical gold nanoparticles, we demonstrated the ability to concentrate electromagnetic energy, incident upon the nanostructure, to within 10s of cubic nanometers (i.e. within the carrier wave near field). Typical radii of localization, based on statistical analysis of NLO signals, spanned the range from 2-5 nm. An important outcome of this research was the capability to spatially localize both linearly and circularly polarized electromagnetic waves. Possible future impacts of this research include the use of plasmonic nanolens structures for ultrafast optical switching with sub-diffraction limited spatial precision and selective plasmon amplification and excitation of specific quantum spin states.

In order to accomplish these research goals, the laser spectroscopy group worked closely with researchers at Air Force Research Laboratory (R.A. Vaia) to identify nanoparticle assembly structures that were top candidates for polarization-specific linear and nonlinear optical localization. As prototypes, we targeted dimeric and trimeric nanolens heterostructures; the trimer nanolens is shown in Figure 1. The trimer structure was formed from a sequence of three gold spheres, arranged in order of decreasing diameter; the diameters used were 130 nm, 80 nm, and 30 nm. During this research, we demonstrated that control over the incident fundamental polarization state yielded selective spatial localization of nonlinear optical signals. For example, excitation using the fundamental wave polarized along the inter-particle axis resulted in second harmonic signals localized between the two smallest spheres forming the nanolens assembly. In contrast, when the fundamental plane of polarization was aligned orthogonal to the inter-particle axis, second harmonic signal intensities were greatest near the largest nanosphere. Importantly, we found that reducing the symmetry from a linear to nonlinear lens impacted our ability to spatial localize nonlinear optical signals to specific regions within the assembly. Our findings have important impacts for nonlinear optical limiting and ultrafast optical switching applications, because they indicate that plamonic nanoassemblies can be used to mediate polarization-specific absorption and frequency up-conversion of incident light. Our results on nanoscale localization of nonlinear optical signals have been published in several journal articles (e.g. *Advanced Materials*, *Nano Letters*, and the *Journal of Physical Chemistry*).

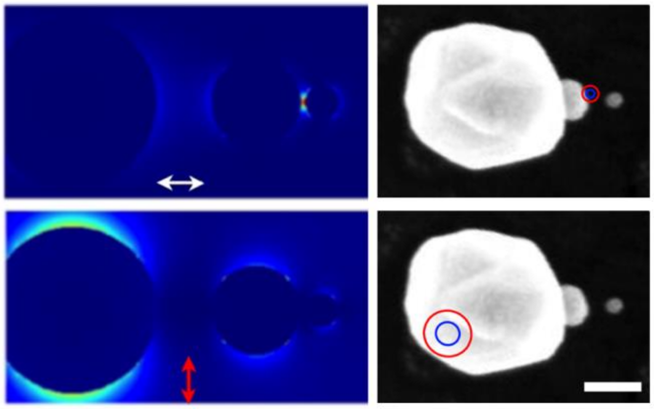

Figure 1. Demonstration of NLO signal localization by plasmonic nanolens structures. (Top, left) Depiction of predicted electromagnetic spatial confinement using a plane polarized fundamental wave with electric field aligned parallel to the nanolens inter-particle axis. These simulations predict spatial focusing of the electromagnetic wave to the region between the two smallest nanospheres forming the trimer assembly. (Top, right) Statistical second harmonic localization results determined to 1σ (blue) and 2 σ (red) confidence levels following excitation parallel to the inter-particle axis. (Bottom, left) Depiction of predicted electromagnetic spatial confinement using a plane polarized fundamental wave with electric field aligned perpendicular to the nanolens inter-particle axis. (Bottom, right) Statistical second harmonic localization results determined to 1σ (blue) and 2 σ (red) confidence levels following excitation perpendicular to the inter-particle axis. In all cases, the experimental data validate theoretical predications of polarization-selective energy localization.

In order to determine if plasmonic nanolens structures could be reliably used for spatial localization of optical signals, it was first necessary to develop laser-based imaging capabilities sensitive enough to measure NLO signals from single nanostructures. Most of our work in this area is published in the *Journal of Chemical Physics* and the *Journal of Physical Chemistry*.

These contributions were a significant factor in my selection as the 2016 Coblentz Awardee. Optical microscopy is indispensable for constructing images of heterogeneous chemical environments and materials, but it is limited to hundreds of nanometers in spatial resolution. A major advantage of NLO imaging is that the input wave parameters can be tailored to generate chemical- and material-specific signals. Although imaging resolution is diffraction limited, the position of a point-source signal can be determined with high accuracy, limited primarily by signal strength. We have shown that NLO enhancement by plasmonic nanoparticles yields images acquired with high temporal resolution (2 frames per second) and a localization accuracy of 1 nm, representing a 160x improvement over the diffraction limit. A manuscript detailing the specifics of the method was published in the *Journal of Chemical Physics (JCP)* and was selected as a JCP Editor's Pick of the Year. This method extends the suite of so-called super-resolution imaging methods to include photobleach-free high-level spectroscopy with rapid throughput. Our 2016 *Journal of Physical Chemistry Letters* paper (*J. Phys. Chem. Lett.* **7**, 765, 2016) describes how chiral nanostructures can be imaged with nanometer spatial accuracy using NLO-detected circular dichroism as an image contrast source.

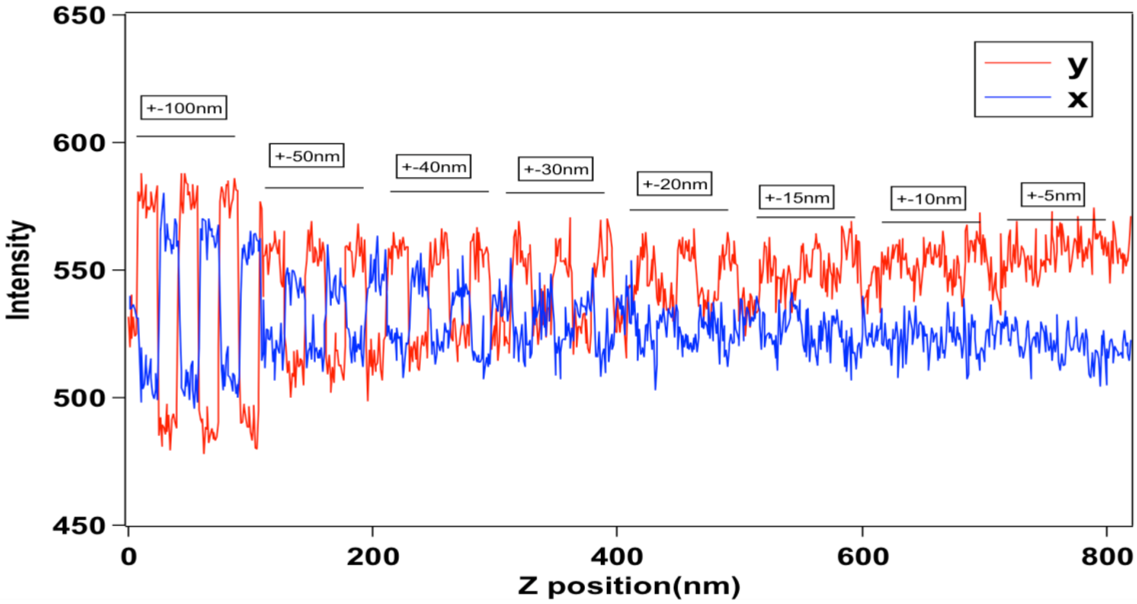

Figure 2. Demonstration of axial localization capabilities. Here, intensity changes following z displacement reflect refinements in z position determination. Saturation of these intensity change points reflects a maximum achievable axial localization for a given signal point source. Here, an iterative change-point method yields saturation at ± 15 nm accuracy, representing significant improvement over what is typically achieved (± 50 nm) when the change-point method is not used.

During the course of the funded program, we extended our 2-D (spatial) methods to include axial localization, thereby providing 3-D super-resolution imaging of nanoparticle assemblies. This was accomplished by introducing different degrees of astigmatism into the *x* and *y* detection arms of the NLO microscope. Analysis of 2-D radial localization accuracies for both *x* and *y* as a function of sample displacement along *z* enables axial localization of signal point source position. This capability is important for distinguishing if plasmonic responses reflect coherent inter-particle modes or nanoparticle-to-substrate coupling. This determination is essential to the accurate development of predictive nanoassembly design models. The method based on using induced astigmatism typically provides z accuracies of ± 50 nm when working at visible wavelengths. My group has also devised a method that combines change-point detection with iterative *z* sample-position scanning that has allowed us to achieve ± 15 nm accuracy in axial location (Figure 2). We anticipate that this level of axial localization will be sufficient for distinguishing substrate from inter-particle coupling contributions to NLO signals obtained from assemblies formed from nanoparticles with approximate-50-nm domain size. These results were published in the *Journal of the Optical Society of America B.*

2. Selective Amplification of Light Polarization States.

We reported the propensity for specific plasmonic assemblies and mode structures to interact selectively with light polarization states. Again, this research was carried out in close collaboration with AFRL scientists at Wright-Patterson Air Force Base. In this work, we showed that relatively simple nanoparticle assemblies formed from two different size nanoparticles could be used to distinguish between right and circularly polarized excitation fields. In this work, we leveraged coherent interference between quadrupolar modes from large nanospheres (diameter ≈ 150 nm) and dipolar modes from comparatively small spheres (diameter ≈ 30 nm). Selective interactions with circularly polarized states were detected using both single-nanostructure two-photon photoluminescence and second harmonic generation measurements. Examples from

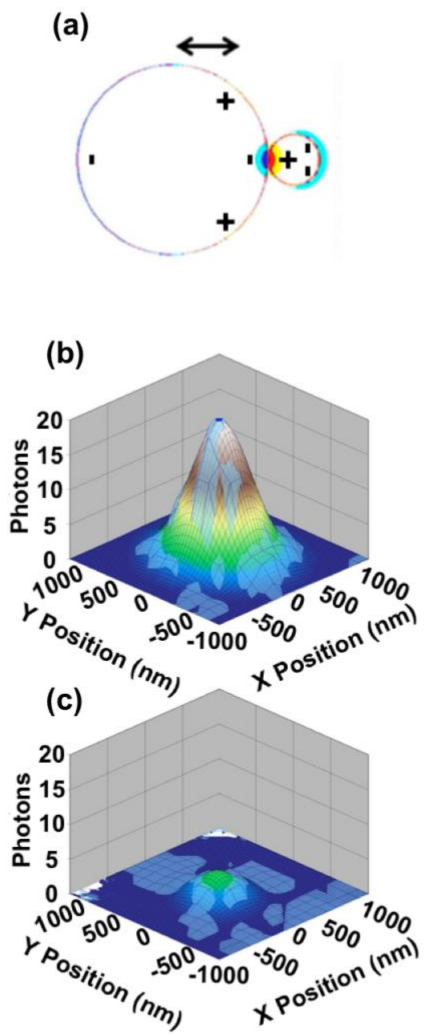

Figure 3. (a) Mode structure describing coherent interference between quadrupolar and dipolar modes resulting from 800-nm excitation of 150 nm and 30 nm gold nanospheres, respectively. 3-D point spread function, describing the number of detected NLO photons resulting from left (b) and right (c) circularly polarized light. The results show the strong propensity for mode-specific polarization-selective optical (and NLO) amplification by plasmonic heterostructures.

NLO-CD imaging of single nanostructures are given in Figure 3.

A key enabling technology that made the measurements possible was the development of single-nanoparticle interferometry measurements using a collinear sequence of phase-stabilized, but orthogonal, laser pulses. We developed a method based on birefringent nonlinear crystals that allowed us to control the temporal delay between the two laser pulses over 2π radians. This method provided attosecond delays for the orthogonal pulses, which made rapid phase cycling of the laser pulses possible in an imaging platform. The resultant phase stability of the inter-pulse delay corresponded to 14 attoseconds. Modulation of the laser polarization state from right to left circularly polarized, from an initially linear state, was achieved by introducing a time delay of ± 667 attoseconds for 800 nm light. This experimental advance provides straightforward, rapid polarization modulation of spectrally broad laser pulses needed for nonlinear optical imaging.

3. Quantification of Plasmon Mode Coherence and Quality Factors.

The efficiency of plasmon optical amplification depends on the mode quality factor, which is related to electronic coherence time; increased coherence time translates to greater amplification efficiency. In principle, plasmon coherence times can be extended for multi-particle assemblies by hybridization of high-order (i.e. non-radiative) modes within the inter-particle resonance. This type of hybridization scheme has the effect of suppressing non-radiative plasmon dephasing. In order to provide inter-particle mode-specific descriptions of plasmon coherence times, my group uses femtosecond time-resolved interferometric nonlinear optical imaging techniques developed in our laboratory. As described in our 2015 *Journal of Physical Chemistry C* Feature Article (**119**, 15779, 2015), these measurements provide both the plasmon-resonance response for a variety of NLO signals and the associated electronic dephasing (coherence) time.

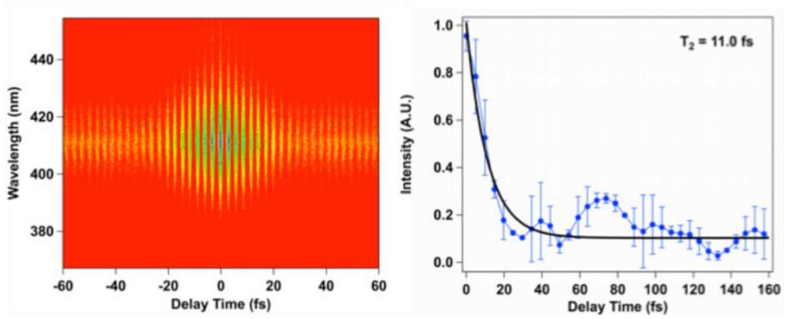

Figure 4. (a) Spectrally and temporally resolved second-harmonic-generation-detected (SHG) interferogram resulting from resonant excitation of a gold nanosphere dimer. (b) Extracted time dependence of plasmon-resonantly-enhanced SHG signal. These time-domain data reflect electronic relaxation dynamics for plasmon-excited nanostructures

An example of a frequency-resolved, SHG-detected interferogram is given in Figure 4a. After the non-resonant SHG instrument response and sample resonance response have been determined, time-resolved data resulting from plasmon-resonant excitation of the nanostructure can be extracted (Figure 4b). As we documented in *J. Phys. Chem. C.* **120**, 4071, 2016, this method accurately captures nanorod-length-to-diameter aspect-ratio-dependent trends in plasmon dephasing for constant-volume nanorods; Figure 5a shows the Fourier amplitudes for resonance responses of three nanorods, and Figure 5b summarizes the dephasing times observed from more than fifty representatives of each resonant sample. As expected, plasmon coherence time is extended as the length-to-diameter aspect ratio increases. Intraband electron scattering with the interband transition is a significant plasmon dephasing mechanism, and rod lengthening allows for energetic decoupling of the plasmon (intraband) excitation from the interband transition.

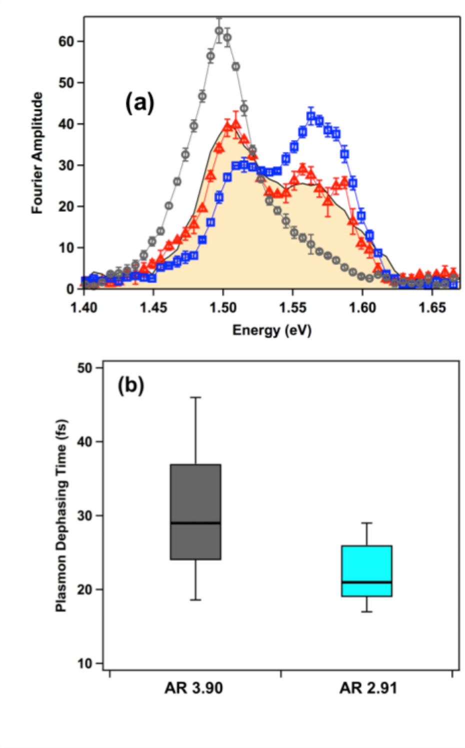

Figure 5. (a) Fourier analysis shows the resonance response of three different nanorods obtained from single-nanoparticle interferometric SHG measurements. The beige-filled spectrum is the laser fundamental. The red spectrum is obtained from a non-resonant nanorod. The blue and gray spectra were obtained from nanorods that were resonant with the high- and low-energy portions of the laser fundamental, respectively. Note that Fourier analysis of the non-resonant sample (red) reproduces the laser spectrum, whereas the blue and gray spectra reveal plasmon resonance frequencies. (b) Summary of extracted electronic dephasing times for resonantly excited nanorods. Taken together, the data show that single-nanoparticle nonlinear optical interferometry can be used for spectroscopic identification of resonant plasmon mode energies and electronic relaxation dynamics.

We have used these interferometric NLO methods to examine mode-specific dynamics of “dolmen” nanorod trimers. The dolmen structure can be treated as two separate but electromagnetically coupled systems: i) a dimer formed by parallel nanorods and ii) a single capping nanorod oriented with its major axis orthogonal to that of the dimer (Figure 6). Numerical simulations indicate that excitation that is plane-polarized parallel to the capping nanorod generates multipolar modes in the dimer, which mix with the longitudinal dipolar resonance of the capping rod. Excitation perpendicular to the capping nanorod results primarily in creation of bright modes localized to the dimer. Our results show that the plasmon coherence times for this nanostructure are very sensitive to the excitation polarization state. The radiative dark-field scattering spectrum obtained for the Dolmen nanorod trimer is given in Figure 7a; the specific trimer assembly is shown in the Figure 7a inset. This spectrum shows a region of scattering transparency near 1.6 eV, which reveals the dark-mode resonance energy. The resonance responses obtained using several different orientations for the sample-incident-excitation angle are shown in Figure 7b. These data were obtained by two-photon photoluminescence imaging and, thus, Fourier analysis reveals the one-photon resonant response for the two-photon absorption process. In good agreement with the scattering data, which showed a dip in radiative intensity at this energy, these data clearly reveal an absorptive, polarization-dependent peak at 1.6 eV. The presence of this peak indicates that the dark mode is strongly coupled to instantaneous nanostructure excitation for specific polarizations. The polarization-dependent dephasing times for this structure are given in Figure 7c. The data reflect an approximately 2x increase in coherence time when the dark mode is excited. In order to test the hypothesis that preserved coherence increases optical amplification, we have correlated the dolmen two-photon

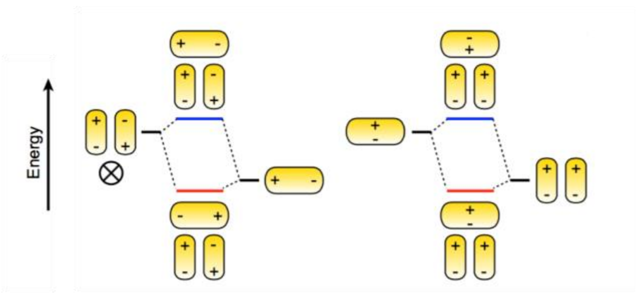

Figure 6. Schematic of inter-particle mode hybridization for "dolmen" nanorod trimers. Depiction of resonant excitations when plane-polarized excitation is oriented parallel (left) and perpendicular (right) to the capping nanorod. Reproduced from *Nano Letters*, **15**, 7666 (2015).

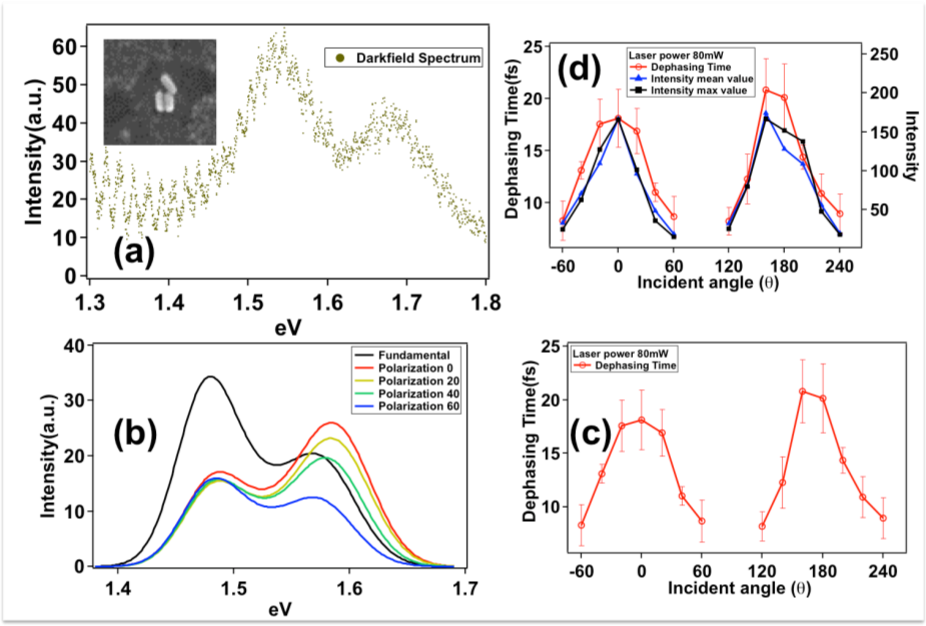

Figure 7. (a) Dark-field scattering spectra obtained from a single dolmen nanorod trimer. The spectra reveal a radiative transparency at 1.6 eV, reflective of the dark-mode energy, superimposed on a broad scattering background. The inset gives the trimer structure.
(b) Excitation-polarization-dependent one-photon resonance response, obtained from Fourier analysis of interferometrically detected two-photon photoluminescence data from the nanostructure depicted in the panel a inset. The data reveal a polarization-dependent absorption peak at 1.6 eV, which suggests the dark mode is strongly coupled to the resonant excitation. (c) Polarization-dependent dephasing times. The strong polarization dependence suggests coupling to non-radiative modes increases plasmon coherence times for the dolmen structures. (d) Comparison of polarization-dependent dephasing times and TPPL signals. The data indicate increased plasmon coherence results in greater optical amplification.

photoluminescence signals to coherence time in Figure 7d. These data show a polarization-dependent 3.5x increase in the intensity of the NLO signal that tracks the coherence time results.

An important outcome of this research is that through interferometric NLO imaging, we were able to identify and implicate specific plasmon modes as efficient energy transducers. Specifically, we were able to demonstrate that selective excitation of "dark" hybrid modes resulted in significant increases in plasmon coherence times and in turn, mode quality factor. Further, we demonstrated that this increased quality factor could be translated to more efficient NLO transduction. Therefore, these research outcomes validate the hypothesis that molecular-like hybridization models can be used to predict the energy conversion efficiency of plasmonic assemblies. In continuing research, my group is investigating how these effects my manifest in other materials, such as atomically thin metals and two-dimensionally confined semiconductors. The significance of the ongoing program is that these plasmonic effects could be observed for systems other than precious metals, and for which significantly smaller volumes of metal are required for function. We are also investigating how interferometric NLO imaging can be used to distinguish plasmon-mediated from thermally driven energy transfer processes at nanoparticle interfaces.

4. Development of ultrafast two-dimensional electronic spectroscopy for measuring strong inter-particle plasmon coupling.

In order to distinguish plasmon-mediated and thermally driven energy transfer processes for nanoparticles, we developed two-dimensional electronic spectroscopy (2DES) capabilities to resolve electronic relaxation dynamics for these systems. As described in the previous section, NLO interferometry gives the plasmon homogenous linewidth and quality factor. In order to understand energy transfer mechanisms involving metals, it is important to measure how this response evolves on the femtosecond to picosecond time scales. Whereas our interferometry methods allow us to resolve the instantaneous response, and plasmon coherence times, 2DES provides the necessary data to resolve relaxation on the femtosecond to picosecond time scales. In addition, the detection of transient cross peaks in 2DES correlation maps allows us to elucidate the role of specific plasmon modes in mediating energy transfer dynamics. During the funding period, my group became the first to publish results on metal nanoparticle electron relaxation using the 2DES method. A summary of this work is given in our recent *Accounts of Chemical Research* article.

Figure 8 illustrates our ability to monitor interfacial energy transfer in plasmonic nanorods. In this specific example, thermally driven interfacial energy transfer from a photo-excited nanoparticle to the surrounding solvent is studied by monitoring the time dependence of the plasmon homogeneous linewidth. The transfer of energy across the nanoparticle/fluid interface results in solvent heating. The increased solvent temperature modified the local dielectric, which affects both the plasmon frequency and linewidth. The latter effect results from modifications to interfacial scattering rates. Therefore, time-dependent measurements of the plasmon frequency and inhomogeneous linewidth provide novel insights into nanoparticle-mediated energy relaxation. It is important to emphasize that the time-dependent homogeneous linewidth, which reveals particle-specific energy transfer mechanisms, could only be obtained from 2DES measurements – these processes could not be visualized using conventional transient spectroscopy methods. In continuing research, we believe this experimental capability will provide valuable insights into plasmon-mode-specific energy transfer and dynamics, interfacial energy transfer, nanoscale thermal conductivities, and heat dissipation. All of these fundamental properties are critical to understand in order to predictively manage energy and heat transfer using nanoparticle-based devices.

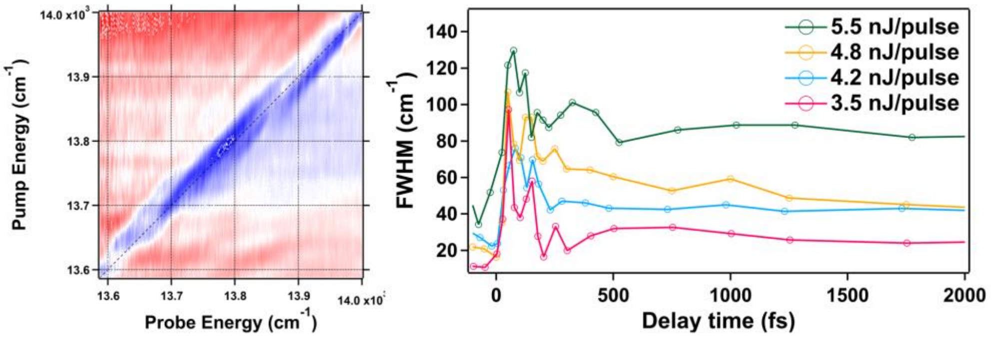

Figure 8. (left) Two-dimensional electronic spectrum obtained from a plasmonic nanorod, acquired at a pump-probe waiting time of 125 fs. The 2DES plot yields the inhomogeneous linewidth along the diagonal. Analysis of the linewidth perpendicular to the diagonal gives the inhomogeneous linewidth at select plasmon frequencies. (right) Time-dependent homogeneous linewidths obtained for different excitation pulse energies. The time dependence of the linewidth monitors nanoparticle-mediated energy transfer dynamics; increasing laser pulse energies correspond to greater electron temperatures.

5. Computational modeling of plasmon dynamics.

The goal of the theoretical part of this effort was to model large nanoparticle trimer structures, including the “Dolman” structures and the “nanolens” trimer nanostructures, in order to provide insights into the optical properties of these systems. Because standard density functional theory (DFT) and time-dependent DFT (TDDFT), even with a jellium approximation, are not capable of treating nanoparticle sizes close to those examined experimentally, alternative approaches have been considered in this work. The most promising approach we have considered is the time-dependent density functional tight binding (TDDFTB) method, which is a semi-empirical method that is parameterized to approximate DFT calculations using the PBE exchange-correlation functional. Using the linear response (LR) formalism, TDDFTB calculations can be applied to silver nanorod and nanorod dimers with thousands of atoms. Tens of thousands of excited states (enough to cover the visible region of the spectrum for these large systems) can be computed. So far, LR-TDDFTB calculations have been utilized for silver nanorod dimers both in a parallel arrangement (modeling two of the three nanorods in the Dolman structure) and in an end-to-end fashion. We have shown that these calculations yield similar physics to related LR-TDDFT calculations, although with somewhat underestimated excitation energies and intensities. Notably, we found that the fractional shifts $(\Delta\square/\square_0)$ for the change in wavelength as a function of the nanorod length in the dimer assemblies does not approach a constant value as previously described in the “plasmon ruler equation”, but instead the functional parameters depend on the nanorod aspect ratio. This shows that the previously accepted plasmon ruler model must be rethought.

We have also leveraged the LR-TDDFTB calculations to examine the diameter dependence of the optical properties of nanorod dimers, which will enable us to extrapolate out to experimental sizes. Again, the LR-TDDFTB calculations can be applied to much larger systems than the corresponding LR-TDDFT calculations, which has permitted quantum mechanical calculations on nanorods with diameters on the order of several nanometers. The shifts in the longitudinal and transverse plasmon energies have been plotted as a function of interparticle distance, and it has been determined that the diameter of the rod affects these distance-shift correlations.

In addition, we have examined a variety of model systems using LR-TDDFT. These model systems represent microscopic versions of the experimental systems that are intended to elucidate some of the underlying physics at play in these systems. These model systems include Dolman-like trimers consisting of three atomic-scale nanorods arranged as two parallel nanorods with a third perpendicular “capping” nanorod. We find that the overall properties of these systems are dominated by the two parallel nanorods, although the third nanorod plays a nonnegligible role in changing the energy and shape of the longitudinal plasmon peak. We have also examined how the optical properties vary with the angle and position of the capping nanorod, which is important because the experimental trimers are rarely perfect. We find that the changes in the optical properties can be generally understood from group theoretical analysis of the symmetry breaking, which suggests that the plasmon hybridization model is appropriate for these systems.

Another system we have studied using LR-TDDFT is heterodimers in which the two parallel nanorods differ in their length. We have analyzed both their dipolar (bright) and quadrupolar (dark) plasmon resonances, and have determined that both the dipolar and quadrupolar plasmons are very sensitive to the interparticle distance, whereas the single-particle states do not noticeably change in energy as the nanorod distance decreases. These systems are of interest for studying energy transfer between wires with different energy levels and for understanding quadrupolar resonances, which are a type of dark plasmon.

We have also employed both LR-TDDFT and LR-TDDFT to examine the optical properties of ‘spherical’ heterodimer systems. These heterodimer systems consist of two icosahedral or FCC nanoparticles with approximately spherical symmetry; these are intended to represent two of the three nanoparticles making up the “snowman” structures. Very little has previously been published on the optical properties of spherical heterodimers, so we are working to elucidate changes in the plasmons as the interparticle distance decreases.

Because LR calculations require the solution of a large number of excited state energies (using matrix eigenvalue solution techniques), these calculations become demanding as system size increases. The real-time (RT) approach for TDDFT and TDDFTB provides an alternative approach to calculating absorption spectra and investigating energy transfer, and can furthermore examine the time-dependence of these energy transfer processes. We have been benchmarking RT vs. LR approaches for silver nanoparticles using both TDDFT and TDDFTB formalisms.

Student training

Overall, six graduate students, one postdoctoral research assistant, and two undergraduate researcher have had the opportunity to learn about various aspects of laser spectroscopy, optical imaging, and theoretical chemistry research, including quantum mechanical methods such as density functional theory and density functional tight binding, and to learn about plasmonic properties of noble metal nanoparticles. The students have also gained experience presenting their research both in conference presentations and in professional journal articles. The students have been exposed to the broader research field through attendance at national and regional conferences.

Dissemination of Research.

The results have been presented at conferences including National, Florida Regional and Midwest Regional American Chemical Society (ACS) meetings. Work has been published in peer-reviewed journals. In particular, our work on experimental laser spectroscopy of plasmonic nanoparticles was described in a Journal of Physical Chemistry C Feature Article, and was featured on two journal covers (Journal of Physical Chemistry C and Advanced Materials Research). Our studies of energy transfer and relaxation dynamics in metal nanostructures were recently published as an invited Accounts of Chemical Research article, and will soon be featured as a Perspective article in an upcoming issue of the Journal of Chemical Physics. Our TDDFTB paper on silver nanorod dimers was selected for ACS Editor’s Choice and for cover art.

Published journal articles:

1. T. Zhao, P. J. Herbert, H. Zheng, K. L. Knappenberger, Jr. “State-Resolved Metal Nanoparticle Dynamics Viewed Through the Combined Lenses of Ultrafast and Magento-Optical Spectroscopies” *Accounts of Chemical Research*, **42**, DOI: 10.1021/acs.accounts.8b00096 (2018).

2. F. Alkan, C. M. Aikens “TD-DFT and TD-DFTB Investigation of the Optical Properties and Electron Structure of Silver Nanorods and Nanorod Dimers.” *J. Phys. Chem. C*, DOI:10.1021/acs.jpcc.8b05196 (2018).

3. T. Zhao, J. W. Jarrett, K. Park, R. A. Vaia, K. L. Knappenberger, Jr. “Axial Point Source Localization using Variable Displacement-Change Point Detection” *Journal of the Optical Society of America B*, **35**, 1140-1148 (2018).

4. P. J. Herbert, U. Mitra, K. L. Knappenberger, Jr. “Variable-Temperature Variable-Field Magnetic Circular Photoluminescence (VTVH-MCPL) Spectroscopy for Electronic-Structure Determination in Nanoscale Chemical Systems” *Optics Letters*, **42**, 4833-4836 (2017).

5. J. W. Jarrett and K. L. Knappenberger, Jr. "Nanoscale Optical Imaging at the Limits of Spatial Accuracy and Temporal Resolution Using Femtosecond NOLES Microscopy" *Science Advances Today*, **2** 25234 (2016).

6. J. W. Jarrett, T. Zhao, J. S. Johnson, X. Liu, P. F. Nealey, R. A. Vaia, and K. L. Knappenberger, Jr. "Plasmon-Mediated Two-Photon Photoluminescence-Detected Circular Dichroism in Gold Nanosphere Assemblies" *The Journal of Physical Chemistry Letters*, **7**, 765-770 (2016).

7. T. Zhao, J. W. Jarrett, J. S. Johnson, K. Park, R. A. Vaia, and K. L. Knappenberger, Jr. "Plasmon Dephasing in Gold Nanorods Studied Using Single-Nanoparticle Interferometric Nonlinear Optical Microscopy" *The Journal of Physical Chemistry C*, **120**, 4071-4079 (2016).

8. X. Liu, S. Biswas, J. W. Jarrett, E. Poutrina, A. Urbas, K. L. Knappenberger, Jr., R. A. Vaia, and P. F. Nealey "Deterministic Construction of Plasmonic Heterostructures in Well-Organized Arrays for Nanophotonic Materials " *Advanced Materials*, **27**, 7314-7319 (2015).

9. J. W. Jarrett, T. Zhao, J. S. Johnson, and K. L. Knappenberger, Jr. "Investigating Plasmonic Structure-Dependent Light Amplification and Electronic Dynamics Using Advances in Nonlinear Optical Microscopy" *The Journal of Physical Chemistry C*, **119**, 15779-15800 (2015).

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Publications in preparation:

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Kenneth L. Knappenberger, Jr.

Program Officer
The AFOSR Program Officer currently assigned to the award

Dr. Michael Berman

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04/01/2015

Reporting Period End Date

03/31/2018

Abstract

The objectives of the research program were centered around the common them of understanding plasmon-mediated and/or controlled energy transfer at the nanoscale. We examined the hypothesis that molecular-based models can be implemented to understand the mechanisms of how plasmonic nanoparticle networks transfer electromagnetic energy, and to determine what nanoparticle structures are most efficient for these applications. The research proceeded through five inter-related themes: 1) super-resolution nanostructure imaging using spatial localization of plasmon-mediated nonlinear optical (NLO) signals; 2) selective-amplification of light polarization states using asymmetric and chiral nanostructures; 3) quantification of plasmon-mode specific electronic coherence times; 4) development of ultrafast two-dimensional electronic spectroscopy for measuring strong inter-particle plasmon coupling; and 5) computational modeling of plasmon dynamics. Taken together, these thrusts provided insight into how the relative arrangement of metal nanostructures in a network determines the optical amplification and polarization selectivity of plasmonic networks. These structure-dependent properties are critical for determining material performance as functional components in light-harvesting applications such as solar-to-electric energy conversion, nonlinear optical limiting technology, ultrafast optical switching, analyte

sensing, and quantum-state-specific excitation, among others. These new insights were obtained through advances in nonlinear optical imaging made in the Knappenberger lab, which include time-resolved (few femtosecond) and 3-D spatially resolved (approximately 1 nm latitudinal and 10 nm axial spatial accuracy) imaging measurements with single-particle sensitivity, and expansion of the computational capabilities of the Aikens group. The research activities advanced through strong synergistic collaboration between Prof. Ken Knappenberger (Florida State University), Christine Aikens (Kansas State University), and Dr. Richard Vaia (AFRL).

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Archival Publications (published) during reporting period:

1. T. Zhao, P. J. Herbert, H. Zheng, K. L. Knappenberger, Jr. "State-Resolved Metal Nanoparticle Dynamics Viewed Through the Combined Lenses of Ultrafast and Magento-Optical Spectroscopies" Accounts of Chemical Research, 42, DOI: 10.1021/acs.accounts.8b00096 (2018).

2. F. Alkan, C. M. Aikens "TD-DFT and TD-DFTB Investigation of the Optical Properties and Electron Structure of Silver Nanorods and Nanorod Dimers." J. Phys. Chem. C, DOI:10.1021/acs.jpcc.8b05196 (2018).

3. T. Zhao, J. W. Jarrett, K. Park, R. A. Vaia, K. L. Knappenberger, Jr. "Axial Point Source Localization using Variable Displacement-Change Point Detection" Journal of the Optical Society of America B, 35, 1140-1148 (2018).

4. P. J. Herbert, U. Mitra, K. L. Knappenberger, Jr. "Variable-Temperature Variable-Field Magnetic Circular Photoluminescence (VTVH-MCPL) Spectroscopy for Electronic-Structure Determination in Nanoscale Chemical Systems" Optics Letters, 42, 4833-4836 (2017).

5. J. W. Jarrett and K. L. Knappenberger, Jr. "Nanoscale Optical Imaging at the Limits of Spatial Accuracy and Temporal Resolution Using Femtosecond NOLES Microscopy" Science Advances Today, 2 25234 (2016).

6. J. W. Jarrett, T. Zhao, J. S. Johnson, X. Liu, P. F. Nealey, R. A. Vaia, and K. L. Knappenberger, Jr. "Plasmon-Mediated Two-Photon Photoluminescence-Detected Circular Dichroism in Gold Nanosphere Assemblies" The Journal of Physical Chemistry Letters, 7, 765-770 (2016).

7. T. Zhao, J. W. Jarrett, J. S. Johnson, K. Park, R. A. Vaia, and K. L. Knappenberger, Jr. "Plasmon Dephasing in Gold Nanorods Studied Using Single-Nanoparticle Interferometric Nonlinear Optical Microscopy" The Journal of Physical Chemistry C, 120, 4071-4079 (2016).

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New discoveries, inventions, or patent disclosures:

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Changes in research objectives (if any):

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Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

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