

Hybrid Plasmonics: New Routes to Imaging, Spectroscopy, and Efficient Energy Flow at the Nanoscale

G. P. Wiederrecht, S. K. Gray, Y. G. Sun, M. Pelton, D. J. Gosztola, J. Hranisavljevic,
Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois

R. Bachelot, J. Plain, M. Juan, P. Royer
*Laboratory for Nanoscale Optical Instrumentation,
University of Technology at Troyes, Troyes, France*

G. Wurtz
*Nano Photonics and Surface Spectroscopies Laboratory
University of North Florida, Jacksonville, Florida*

W. Dickson, D. O'Connor, P. Evans, W. Hendren, R. Atkinson, R. Pollard, and A. Zayats
*Center for Nanostructured Media
The Queen's University of Belfast, United Kingdom*

Scientific Thrust Area

Experimental nanophotonics.

Research Achievement

This work focuses on creating novel electronic and optical states in hybrid nanomaterials in order to provide new routes for the imaging and manipulation of optical energy at the nanoscale. The motivation for this work is that basic studies in nanophotonics can reveal optical phenomena that are useful for a range of critical technologies including energy collection and conversion, next generation optics, and ultrasensitive spectroscopies.

Plasmonic metal nanostructures are excellent systems in which to study nanophotonics processes, because they support evanescent optical fields with spatial features well below the diffraction limit of dielectric materials. The strong field confinement and field enhancement at the metal-dielectric interface, combined with strong tunability of the plasmonic properties with shape, size, composition, and environment, have produced a wealth of advances, particularly in enhanced spectroscopies (e.g. surface enhanced Raman scattering and fluorescence) and nanoscale optical circuitry. Plasmonic materials therefore serve as the “core” of our hybrid nanostructures.

The strongly localized fields that serve as the foundation of plasmonics research can be used to couple to, and modify, plasmonic, excitonic, and molecular excitations in hybrid materials. Due to the short-range nature of evanescent interactions in nanostructures, these coupling interactions can be strong and do not necessarily have analogs in bulk materials. In the research described here, we have utilized plasmonic coupling to both isolated molecular excitations and excitonic organic structures to realize (a) new routes to sub-wavelength imaging and (b) altered energy flow in nanostructures. One example for each is given here.

For the imaging example, plasmonic nanoparticles are covered with an azo-dye polymer film. The azo-dye is chosen to undergo a light-induced cis-trans isomerization when excited at the plasmon resonance energy. Repetitive isomerizations produce mass transport of the polymer out of the evanescent near-field zone, thereby producing holes in the polymer film that reflect the spatial features of the evanescent field. These can be

detected through atomic force microscopy with a resolution of approximately 20 nm. We have used this mass transport phenomenon to image optical near-fields of plasmonic bowtie antennae and nanorods. Theoretical work clarifies the light-molecule interactions that produce this effect.

For the second example, ultrafast relaxational processes in assemblies of strongly interacting nanorods are studied (Figure 1). Here, we characterize the modification of plasmon-mode relaxation processes when coupled to molecular excitonic materials placed within the interstices of the rods. We find that a mixed plasmon-exciton state is produced, and that variability in the plasmon-exciton coupling produces strong changes in the relaxation dynamics.

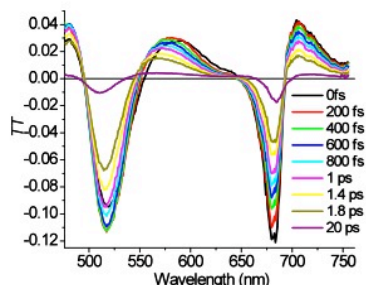
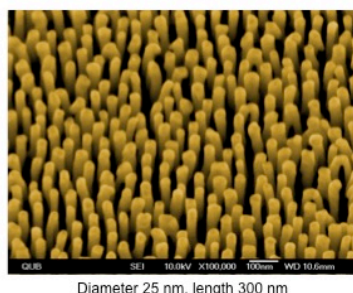


Figure 1. The plasmonic Au nanorod array and ultrafast transient absorption spectra are shown. Hybridizing with molecular excitonic materials strongly modifies the plasmonic modes.

Future Work

Future work will be to realize new hybrid materials and nanostructures with novel optical properties and altered energy flow phenomena, which also enable external control over that energy flow. Specific targets at this time are electronically responsive metal nanoparticle/liquid crystalline materials. Future work will be performed in continued collaboration with the theory and modeling group and will also use the advanced lithography capabilities at the CNM.

Publications

- Plasmonic electromagnetic hot spots temporally addressed by photoinduced molecular displacement. M. L. Juan, J. Plain, R. Bachelot, A. Vial, P. Royer, S. K. Gray, G. P. Wiederrecht, *J. Phys. Chem. A* **113**, 4647 (2009).
- Fabrication of metallic nano-slit waveguides with sharp bends. M. Lu, L. E. Ocola, S. K. Gray, G. P. Wiederrecht, *J. Vac. Sci. & Tech. B* **26**, 2151 (2008).
- Stochastic model for photoinduced surface relief grating formation through molecular transport in polymer films. M. L. Juan, J. Plain, R. Bachelot, P. Royer, S. K. Gray, G. P. Wiederrecht, *Appl. Phys. Lett.* **93**, 153304 (2008).
- Ultrafast hybrid plasmonics. G. P. Wiederrecht, G. A. Wurtz, A. Bouhelier, *Chem. Phys. Lett.* **461**, 171 (2008).
- Comparative study on the growth of silver nanoplates on GaAs substrates by electron microscopy, synchrotron X-ray diffraction, and optical microscopy. Y. G. Sun, H. F. Yan, and G. P. Wiederrecht, *J. Phys. Chem. C* **112**, 8928 (2008).
- Near-field polarization effects in molecular-motion-induced photochemical imaging. C. Hubert, R. Bachelot, J. Plain, S. Kostcheev, G. Lerondel, M. Juan, P. Royer, S. Zou, G. C. Schatz, G. P. Wiederrecht, and S. K. Gray. *J. Phys. Chem. C* **112**, 4111 (2008).
- Surfactantless synthesis of silver nanoplates with rough surfaces and their application in SERS. Y. G. Sun and G. P. Wiederrecht, *Small* **3**, 1964 (2007). (cover article)
- Surface plasmon interference excited by tightly focused laser beams. A. Bouhelier, F. Ignatovich, A. Bruyant, C. Huang, G.C. Frans, J. Weeber, A. Dereux, G.P. Wiederrecht, and L. Novotny, *Opt. Lett.* **32**, 2535 (2007).
- Control of molecular energy redistribution pathways via surface plasmon gating. G. P. Wiederrecht, J.E. Hall, and A. Bouhelier, *Phys. Rev. Lett.* **98**, 083001 (2007).
- Heterodyne method of apertureless near-field scanning optical microscopy on periodic gold nanowells. J. E. Hall, G.P. Wiederrecht, S.K. Gray, S. Chang, S. Jeon, J.A. Rogers, R. Bachelot, P. Royer, *Opt. Express* **15**, 4098 (2007).