

## Electron Optics of Self-Assembled Plasmonic Nanocomposite Metamaterials

D.Keith Roper<sup>a,b</sup>, D. DeJarnette<sup>b</sup>, J. Norman<sup>c</sup> and G. Forcherio<sup>b</sup>

<sup>a</sup>Department of Chemical Engineering, University of Arkansas, Fayetteville, AR 72701, [dkroper@uark.edu](mailto:dkroper@uark.edu)

<sup>b</sup>Microelectronics and Photonics Graduate Program, University of Arkansas, Fayetteville, AR 72701

<sup>c</sup>Materials Department, University of California Santa Barbara, Santa Barbara, CA 93106

Plasmonic nano-antennas, which couple optics and electronics, are of increasing interest as waveguides, emitters, and interconnects in semiconductor devices, particularly in the near infrared region [1,2]. Dynamic enhancement of opto-electronic coupling could fundamentally impact performance of plasmonic nanoantenna semiconductor devices integrated into applications as diverse as biomedical theranostics, synthetic biology, and sustainable energy [3]. Fundamentally, quantized photon-exciton coupling is the source of electron-hole pairs in semiconductor photovoltaics, induced charge transfer in ordered DNA chains, and distance-dependent Forster resonance energy transfer in spectroscopic molecular rulers [4].

Our lab has recently distinguished relative contributions of quantized plasmon polarizabilities and photon diffraction to extraordinary opto-electronic coupling in ordered metal-ceramic and metal-polymeric nanocomposite metamaterials (see Fig 1) [5,6]. Metamaterials exhibit tunable electromagnetic functionality -- from simple iridescence in butterfly wings to radiofrequency cloaking -- due to coherent interference from multidimensional structuring of suitable condensed-matter composites. We showed that surface energy driven self-assembly of plasmonic metamaterials can occur by electroless nanosphere synthesis on nanolithographed anti-gecko lattices [7]. This novel result has been extended to modulate nanoscale photodynamic, hydraulic, and redox potentials to allow ionic precursors to nucleate into various nanostructured isoforms including spheres, island films, and clusters with various substrates (see Fig. 4) [8-10]. Recent progress has been made in distinguishing coherent and incoherent optical re-radiation and thermal dissipation from plasmonic nano-antennas in devices by correlating experimental and theoretical results [11].

Description and design of dynamical electron optics in systems and devices has been obstructed to date by expense and complexity of available numerical computations and effective media approximations [12,13]. Our group has developed and validated a suite of rapid approximate methods which synthesize tractable descriptions of near-field polarizability and far-field modal interference to efficiently describe energetics of electron optic coupling in plasmonic metamaterials (See Fig 2) [5,6,14]. In particular, this approach supports quantitative attribution of effects of physicochemical and geometrical features of nanocomposite metamaterials on quantum and continuum interactions that exhibit predictable Fano resonances and thermal dissipation in near infrared regions (see Fig 3) [15]. A recent extension of this approach to geometric optics supported accurate prediction and characterization of linear and non-linear influences, respectively, of plasmonic nanocomposites in microscale systems [13].

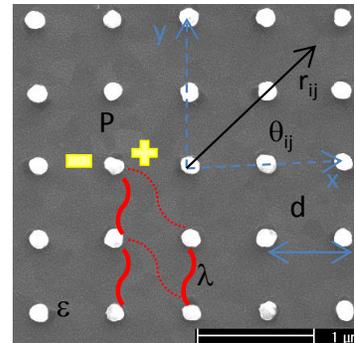


Fig 1. Describing self-assembled gold nanoparticle plasmonic metamaterial.

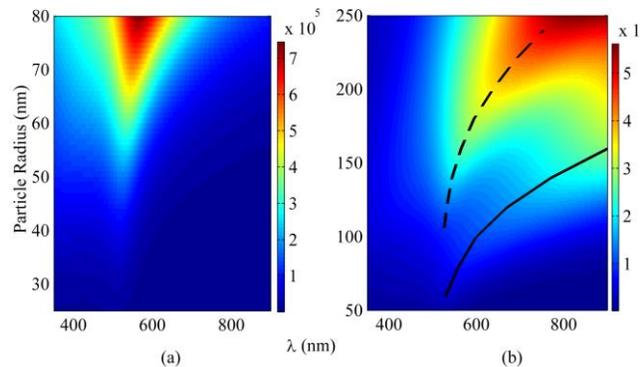


Fig 2. Frequency-dependent dipole and quadrupole polarizabilities for various gold nanoparticles [6].

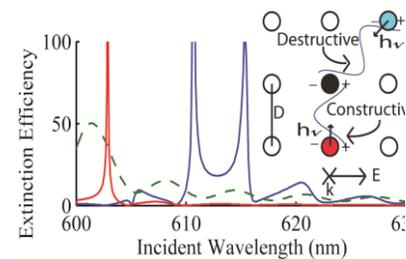


Fig 3. Phase interference modulates Fano resonant energy.

Characterization of fabricated metamaterials and validation of their fundamental descriptions has been facilitated in our lab by microspectroscopies (x-ray photoelectron; transmission UV; and Raman) and transmission/scanning electron and optical microscopies. Advances in these physicochemical characterization methods have supported measurable improvements in opto-electronic interactions in nano-scale metallic particles and films (see Fig. 4) [8,9,13,16]. These advances in modeling, fabrication, characterization, and systems integration are important milestones toward integrating electromagnetically active nanocomposite metamaterials into next-generation semiconductor devices that support micro-to-nano-scale electronics, tele-communications, with extensions to molecular engineering, disease diagnosis, personalized therapies, and energy harvesting [17].

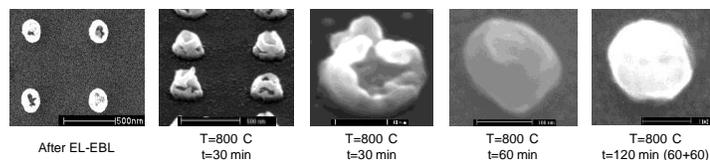


Fig 4. Thermally tunable metalloceramic nanomorphs.

## References

- [1] J. A. Schuller, E. S. Barnard, W. Cai, Y. C. Jun, J. S. White, and M. L. Brongersma, "Plasmonics for extreme light concentration and manipulation," *Nat. Mater.* 9, 193–204 (2010). (Journal Article)
- [2] H. A. Atwater and A. Polman, "Plasmonics for improved photovoltaic devices," *Nat. Mater.* 9, 205–213 (2010). (Journal Article)
- [3] D.K. Roper, W. Ahn, B. Taylor, Y. D'Asen, "Enhanced spectral sensing by electromagnetic coupling with localized surface plasmons on subwavelength structures," *IEEE Sensors Journal* (2010) 10(3) 531-540. (Journal Article)
- [4] R. T. Hill, J. J. Mock, A. Hucknall, S. D. Wolter, N. M. Jokerst, D. R. Smith, and A. Chilkoti, "Plasmon ruler with Angstrom length resolution," *ACS Nano* 6, 9237–9246 (2012). (Journal Article)
- [5] D. Dejarnette, J. Norman, D.K. Roper, "Spectral patterns underlying polarization-enhanced diffractive interference are distinguishable by complex geometry," *Appl. Phys. Lett.* (2012) 101(18) 193104. (Journal Article)
- [6] D. Dejarnette, D.K. Roper, B. Harbin, "Geometric effects on far-field coupling between multipoles of nanoparticles in square arrays," *JOSA B.* (2012) 29(1) 88-100. (Journal Article)
- [7] W. Ahn and D. K. Roper, "Periodic nanotemplating by selective deposition of electroless gold island films on particle-lithographed dimethyldichlorosilane layers," *ACS Nano* (2010) 4(7) 4181-4189. (Journal Article)
- [8] J. Dunklin, G. Forcherio, K. Berry, and D.K. Roper, "Asymmetric reduction of gold nanoparticles into thermoplasmonic polydimethylsiloxane thin films," *ACS Appl. Mat. Interf.* (2013) DOI: 10.1021/am4018785 Published (Web) Aug 9, 2013. (Journal Article)
- [9] K. Berry, A. Russell, P. Blake, D.K. Roper, "Gold NP reduced *in situ* and dispersed in polymer thin films: optical and thermal properties," *Nanotechnology.* (2012) 23, 375703. (Journal Article)
- [10] G. Jang, P. Blake, and D.K. Roper, "Rate-limited electroless gold thin film growth: a real-time study," *Langmuir.* (2013) 29(18) 5476-5486. DOI: 10.1021/la304154u (Journal Article)
- [11] G. Forcherio, and D.K. Roper, "Optical attenuation of plasmonic nanocomposites within photonic devices," *Appl. Optics* (2013) 52(25) 6417-6427. (Journal Article)
- [12] K. Yee, "Numerical solution of initial boundary value problems involving Maxwell's equations in isotropic media," *IEEE Trans. Antennas Propag.* 14, 302–307 (1966). (Journal Article)
- [13] B. T. Draine and P. J. Flatau, "Discrete-dipole approximation for periodic targets: theory and tests," *J. Opt. Soc. Am. A* 25, 2693–2703 (2008). (Journal Article)
- [14] D.K. Roper, P. Blake, D. DeJarnette, B. Hardin. "Plasmon coupling enhanced in nanostructured chem/bio sensors." In *Nano-Plasmonics: Advanced Device Applications*. J.W.M. Chon and K. Iniewski, Eds. *CRC Press* (2013). *In press.* (Book Chapter)
- [15] D.K. Roper, W. Ahn, M. Hoepfner, M. "Microscale heat transfer transduced by surface plasmon resonant gold nanoparticles," *J Phys Chem C.* (2007) 111(9) 3636-3641. (Journal Article)
- [16] G. Jang and D.K. Roper, "Continuous flow electroless plating enhances optical features of Au films and nanoparticles," *J. Phys. Chem C.* (2009) 113:19228-19236. (Journal Article)
- [17] D.K. Roper and S. Nakra, "Adenovirus type 5 intrinsic adsorption rates measured by surface plasmon resonance," *Anal Biochem.* 348 (2006) 75-83. (Journal Article)