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a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			Naomi Halas
					19b. TELEPHONE NUMBER 713-348-5612

RPPR Final Report
as of 16-Dec-2021

Agency Code: 21XD

Proposal Number: 61796CHMUR

Agreement Number: W911NF-12-1-0407

INVESTIGATOR(S):

Name: Naomi Halas halas@rice

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Principal: Y

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DUNS Number: 050299031

EIN: 741109620

Report Date: 19-Jan-2020

Date Received: 16-Dec-2021

Final Report for Period Beginning 20-Aug-2012 and Ending 19-Oct-2019

Title: Coherent Effects in Hybrid Nanostructures for Lineshape Engineering of Electromagnetic Media

Begin Performance Period: 20-Aug-2012

End Performance Period: 19-Oct-2019

Report Term: 0-Other

Submitted By: Naomi Halas

Email: halas@rice.edu

Phone: (713) 348-5612

Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 4

STEM Participants: 10

Major Goals: The MURI: Coherent Effects in Hybrid Nanostructures for Lineshape Engineering of Electromagnetic Media was started with the on the following goals:

- to understand, design, and optimize standalone nanoparticles and their assemblies for transparency windows at specific frequencies;
- collaborative studies on morphologies resulting in tailored spectral transparency windows;
- to develop new, low-loss, lower-cost, benign, metallic and semiconductor nanoparticles and nanocomplexes to realize these effects;
- to perform optical measurements from the visible to the far-IR regions of the spectrum, to characterize and optimize engineered linewidths in these systems;
- to advance the surface chemistry of nanoassemblies, facilitating fluid or vapor phase particle dispersal for evaluation of particulate optical properties.

As the MURI progressed, we focused the nanocrystal synthesis to aluminum-based nanocrystals and their modifications and developed algorithms and techniques to image through scattering media.

- Ligand-directed growth of Al reduced-symmetry NCs, to extend Al NC resonances into and across the infrared region of the spectrum;
- Catalyst variation for controlled-aspect-ratio Al NC nanorods and large-aspect-ratio nanowires, to examine the long-wavelength properties and capabilities of large aspect-ratio nanorods;
- Seed-mediated growth by Ag nanostructures: exploiting the lattice-matching between Ag and Al to synthesize reduced-symmetry Al nanostructures such as nanoplates (in collaboration with Nanocomposix);
- H₂O-based separation procedures for coated Al NC and NRs, critical for all chemically synthesized Al nanoparticle, enabled by our coatings developed in the last funding cycle;
- Incorporation of new materials for added functionality and stability: Ti doping of Al NCs (TiAl cores); Al-doped TiO₂ coating layers; growth of TiN coatings around Al NCs for added infrared capabilities along with high-temperature durability
- Imaging through scattering media

Accomplishments: See attached file

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Training Opportunities: Graduate students supported by the grant graduated with a PhD degree and are working in academia or industry.

Benjamin Cerjan: (PhD) postdoctoral associate at Rice (ARL LUCI grant support)

Benjamin Clark: (PhD) working at Nanocomposix

Hossein Robatjazi: (PhD) won the Arnold Beckman award in 2019, Postdoctoral scholar at University of California Santa Barbara

Results Dissemination: Nothing to Report

Honors and Awards: Naomi Halas:

2020 Doctor of Science honoris causa, Université de technologie de Troyes (postponed until 2021)

2019 Fellow, Royal Society of Chemistry

2019 ACS Nano Lectureship Award

2019 Highly Cited Researcher, Clarivate (Materials Science)

2019 Hershel Rich Invention Award: Antenna-Reactor Effect (Rice University)

2019 Spiers Memorial Award, Royal Society of Chemistry

2019 ACS Award in Colloid Chemistry

Hossein Robatjazi:

2019 Arnold O. Beckman Postdoctoral Fellowship

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI

Participant: Naomi J Halas

Person Months Worked: 1.00

Project Contribution:

National Academy Member: Y

Funding Support:

Participant Type: Co PD/PI

Participant: Peter Nordlander

Person Months Worked: 1.00

Project Contribution:

National Academy Member: N

Funding Support:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Arash Ahmadvand

Person Months Worked: 3.00

Project Contribution:

National Academy Member: N

Funding Support:

Participant Type: Graduate Student (research assistant)

Participant: Arzeena Ali

Person Months Worked: 6.00

Project Contribution:

National Academy Member: N

Funding Support:

RPPR Final Report
as of 16-Dec-2021

Participant Type: Graduate Student (research assistant)
Participant: Benjamin Cerjan
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Benjamin Clark
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Minghe Lou
Person Months Worked: 10.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Ewa Nowara
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: David Renard
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Hossein Robatjazi
Person Months Worked: 10.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Michael Semmlinger
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
National Academy Member: N

RPPR Final Report as of 16-Dec-2021

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Manoj Sharma
Person Months Worked: 12.00
Funding Support:
Project Contribution:
National Academy Member: N

Participant Type: Co PD/PI
Participant: Ashok Veeraraghavan
Person Months Worked: 1.00
Funding Support:
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Lin Yuan
Person Months Worked: 10.00
Funding Support:
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Runmin Zhang
Person Months Worked: 2.00
Funding Support:
Project Contribution:
National Academy Member: N

ARTICLES:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Nature

Publication Identifier Type: DOI

Publication Identifier: 10.1038/nature12401

Volume: 500

Issue: 7460

First Page #: 59

Date Submitted:

Date Published:

Publication Location:

Article Title: Stretchable nanoparticle conductors with self-organized conductive pathways

Authors:

Keywords: Flexible electronics,

Abstract: Research in stretchable conductors is fuelled by diverse technological needs. Flexible electronics, neuroprosthetic and cardiostimulating implants, soft robotics and other curvilinear systems require materials with high conductivity over a tensile strain of 100 per cent (refs 1–3). Furthermore, implantable devices or stretchable displays⁴ need materials with conductivities a thousand times higher while retaining a strain of 100 per cent. However, the molecular mechanisms that operate during material deformation and stiffening make stretchability and conductivity fundamentally difficult properties to combine. The macroscale stretching of solids elongates chemical bonds, leading to the reduced overlap and delocalization of electronic orbitals⁵. This conductivity–stretchability dilemma can be exemplified by liquid metals, in which conduction pathways are retained on large deformation but weak interatomic bonds lead to compromised strength. The best-known stretchable conductors use polymer

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Journal of the American Chemical Society

Publication Identifier Type: DOI

Publication Identifier: 10.1021/ja3066336

Volume: 134

Issue: 36

First Page #: 15114

Date Submitted:

Date Published:

Publication Location:

Article Title: Self-Assembly of Chiral Nanoparticle Pyramids with Strong

Authors:

Keywords: Chiral, DNA assembly, gold nanoparticles, tetrahedral,

Abstract: Chirality at the nanometer scale represents one of the most rapidly developing areas of research. Self-assembly of DNA? nanoparticle (NP) hybrids enables geometrically precise assembly of chiral isomers. The concept of a discrete chiral nanostructure of tetrahedral shape and topology fabricated from four different NPs located in the corners of the pyramid is fundamental to the field. While the first observations of optical activity of mixed pyramidal assemblies were made in 2009 (Chen, W.; et al. Nano Lett. 2009, 9, 2153?2159), further studies are difficult without finely resolved optical data for precisely organized NP pyramidal enantiomers. Here we describe the preparation of a family of self-assembled chiral pyramids made from multiple metal and/or semiconductor NPs with a yield as high as 80%. Purposefully made R- and S-enantiomers of chiral pyramids with four different NPs from three different materials displayed strong chiroptical activity, with anisotropy g-factors as high as 1.

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Scientific Reports

Publication Identifier Type: DOI

Publication Identifier: 10.1038/srep01934

Volume: 3

Issue: 1934

First Page #: 0

Date Submitted:

Date Published:

Publication Location:

Article Title: Chiral plasmonics of self-assembled nanorod dimers

Authors:

Keywords: Molecular self assembly, Nanoparticles, Biomimetics

Abstract: Chiral nanoscale photonic systems typically follow either tetrahedral or helical geometries that require four or more different constituent nanoparticles. Smaller number of particles and different chiral geometries taking advantage of the self-organization capabilities of nanomaterials will advance understanding of chiral plasmonic effects, facilitate development of their theory, and stimulate practical applications of chiroplasmonics. Here we show that gold nanorods self-assemble into side-by-side orientated pairs and "ladders" in which chiral properties originate from the small dihedral angle between them. Spontaneous twisting of one nanorod versus the other one breaks the centrosymmetric nature of the parallel assemblies. Two possible enantiomeric conformations with positive and negative dihedral angles were obtained with different assembly triggers. The chiral nature of the angled nanorod pairs was confirmed by 4p full space simulations and the first example of single-particle CD

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Nano Letters

Publication Identifier Type: DOI

Publication Identifier: 10.1021/nl402231z

Volume: 0

Issue: 0

First Page #: 0

Date Submitted:

Date Published:

Publication Location:

Article Title: 3-D Plasmonic Nanoclusters

Authors:

Keywords: nanoparticle clusters, metamaterial, optical properties

Abstract: Assembling nanoparticles into well-defined structures is an important way to create and tailor the optical properties of materials. Most advances in metamaterials research to date have been based on structures fabricated in two-dimensional planar geometries. Here, we show an efficient method for assembling noble metal nanoparticles into stable, three-dimensional clusters, whose optical properties can be highly sensitive or remarkably independent of cluster orientation, depending on particle number and cluster geometry. Some of the clusters, such as tetramers and icosahedra, could serve as the optical kernels for metafluids, imparting metamaterial optical properties into disordered media such as liquids, glasses, or plastics, free from the requirement of nanostructure orientation.

Distribution Statement: 1-Approved for public release; distribution is unlimited.

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: ACS Sustainable Chemistry & Engineering

Publication Identifier Type: DOI

Publication Identifier: 10.1021/sc400042h

Volume: 1

Issue: 0

First Page #: 833

Date Submitted:

Date Published:

Publication Location:

Article Title: Adsorption of a Protein Monolayer via Hydrophobic Interactions Prevents Nanoparticle Aggregation under Harsh Environmental Conditions

Authors:

Keywords: Gold nanoparticles, Surface plasmon, Bovine serum albumin, Protein corona, Correlation spectroscopy, Diffusion

Abstract: We find that citrate-stabilized gold nanoparticles aggregate and precipitate in saline solutions below the NaCl concentration of many bodily fluids and blood plasma. Our experiments indicate that this is due to complexation of the citrate anions with Na⁺ cations in solution. A dramatically enhanced colloidal stability is achieved when bovine serum albumin is adsorbed to the gold nanoparticle surface, completely preventing nanoparticle aggregation under harsh environmental conditions where the NaCl concentration is well beyond the isotonic point. Furthermore, we explore the mechanism of the formation of this albumin "corona" and find that monolayer protein adsorption is most likely ruled by hydrophobic interactions. As for many nanotechnology-based biomedical and environmental applications, particle aggregation and sedimentation are undesirable and could substantially increase the risk of toxicological side effects; the formation of the BSA corona presented here provides a low-cost bioc

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Journal of the American Chemical Society

Publication Identifier Type: DOI

Publication Identifier: 10.1021/ja312694g

Volume: 135

Issue: 9

First Page #: 0

Date Submitted:

Date Published:

Publication Location:

Article Title: Surface-Enhanced Infrared Absorption Using Individual Cross Antennas Tailored to Chemical Moieties

Authors:

Keywords: Surface Enhanced Infrared Absorption, Tunable crossed nanoantennas, Fano Resonance,

Abstract: The development of antenna structures for surface-enhanced infrared absorption spectroscopy (SEIRA) is a topic of intense and growing interest for extending IR spectroscopy to zeptomolar quantities and ultimately to the single-molecule level. Here we show that strong infrared spectroscopic enhancements can be obtained from individual gold nanoantennas using conventional IR spectrometric sources. The antenna structure dimensions can be tuned to enhance the IR modes of specific chemical moieties. Simulations of the electric field intensity in the antenna junction region reveal a maximum SEIRA enhancement factor of more than 12 000. These findings open new opportunities for analyzing IR vibrations of exceptionally small quantities of molecules using widely accessible light sources.

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Peer Reviewed: Y

Publication Status: 1-Published

Journal: Nano Letters

Publication Identifier Type: DOI

Publication Identifier: 10.1021/nl400196z

Volume: 13

Issue: 4

First Page #: 1687

Date Submitted:

Date Published:

Publication Location:

Article Title: Embedding Plasmonic Nanostructure Diodes Enhances Hot Electron Emission

Authors:

Keywords: Plasmon; nanoparticle; nanowire; hot electron; embedded; Schottky

Abstract: When plasmonic nanostructures serve as the metallic counterpart of a metal–semiconductor Schottky interface, hot electrons due to plasmon decay are emitted across the Schottky barrier, generating measurable photocurrents in the semiconductor. When the plasmonic nanostructure is atop the semiconductor, only a small percentage of hot electrons are excited with a wavevector permitting transport across the Schottky barrier. Here we show that embedding plasmonic structures into the semiconductor substantially increases hot electron emission. Responsivities increase by 25× over planar diodes for embedding depths as small as 5 nm. The vertical Schottky barriers created by this geometry make the plasmon-induced hot electron process the dominant contributor to photocurrent in plasmonic nanostructure-diode-based devices.

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Publication Type: Journal Article

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Publication Status: 1-Published

Journal: Nano Letters

Publication Identifier Type: DOI

Publication Identifier: 10.1021/nl4014887

Volume: 13

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Date Submitted:

Date Published:

Publication Location:

Article Title: Near-Field Mediated Plexcitonic Coupling and Giant Rabi Splitting in Individual Metallic Dimers

Authors:

Keywords: Plexcitons; surface plasmons; molecular excitons; Rabi splitting; dark-field spectroscopy; individual hybrid nanostructures

Abstract: Strong coupling between resonantly matched localized surface plasmons and molecular excitons results in the formation of new hybridized energy states called plexcitons. Understanding the nature and tunability of these hybrid nanostructures is important for both fundamental studies and the development of new applications. We investigate the interactions between J-aggregate excitons and single plasmonic dimers and report for the first time a unique strong coupling regime in individual plexcitonic nanostructures. Dark-field scattering measurements and finite-difference time-domain simulations of the hybrid nanostructures show strong plexcitonic coupling mediated by the near-field inside each dimer gap, which can be actively controlled by rotating the polarization of the optical excitation. The plexciton dispersion curves, obtained from coupled harmonic oscillator models, show anticrossing behavior at the exciton transition energy and giant Rabi splitting ranging between 230 and 400 meV.

T

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Peer Reviewed: Y

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Journal: Nano Letters

Publication Identifier Type: DOI

Publication Identifier: 10.1021/nl303517v

Volume: 12

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Date Submitted:

Date Published:

Publication Location:

Article Title: Aluminum Plasmonic Nanoantennas

Authors:

Keywords: Aluminium, UV plasmonics, cathodoluminescence,

Abstract: The use of aluminum for plasmonic nanostructures opens up new possibilities, such as access to short-wavelength regions of the spectrum, complementary metal–oxide–semiconductor (CMOS) compatibility, and the possibility of low-cost, sustainable, mass-producible plasmonic materials. Here we examine the properties of individual Al nanorod antennas with cathodoluminescence (CL). This approach allows us to image the local density of optical states (LDOS) of Al nanorod antennas with a spatial resolution less than 20 nm and to identify the radiative modes of these nanostructures across the visible and into the UV spectral range. The results, which agree well with finite difference time domain (FDTD) simulations, lay the groundwork for precise Al plasmonic nanostructure design for a variety of applications.

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Journal: The Journal of Physical Chemistry Letters

Publication Identifier Type: DOI

Publication Identifier: 10.1021/jz4004137

Volume: 4

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Date Submitted:

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Article Title: Geometric Dependence of the Line Width of Localized Surface Plasmon Resonances

Authors:

Keywords: Plasmonics, Optical Materials, and Hard Matter

Abstract: For the same number of electrons and plasmon frequencies, longitudinal plasmon resonances in metallic nanorods exhibit narrower line widths than plasmon modes in spherical particles. We show that this property is a general feature of high aspect ratio nanostructures and can be explained very simply by incorporating retardation effects into a harmonic oscillator model. The origin of the effect is dynamic depolarization, which renormalizes the mass of the electrons and the oscillating electron liquid. The scattering spectrum derived from our model agrees very well with FDTD simulations. Because plasmon damping determines many important features and applications of LSPR, such as the Q factor of plasmonics devices and the magnitude of the induced field enhancements, our study will play an important role for the design of nanostructures with narrow plasmon resonances.

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Journal: Nano Letters

Publication Identifier Type: DOI

Publication Identifier: 10.1021/nl4001184

Volume: 13

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First Page #: 1317

Date Submitted:

Date Published:

Publication Location:

Article Title: Phosphorus-Doped Silicon Nanocrystals Exhibiting Mid-Infrared Localized Surface Plasmon Resonance

Authors:

Keywords: Silicon nanocrystals, localized surface plasmon resonance, doping

Abstract: Localized surface plasmon resonances (LSPRs) enable tailoring of the optical response of nanomaterials through their free carrier concentration, morphology, and dielectric environment. Recent efforts to expand the spectral range of usable LSPR frequencies into the infrared successfully demonstrated LSPRs in doped semiconductor nanocrystals. Despite silicon's importance for electronic and photonic applications, no LSPRs have been reported for doped silicon nanocrystals. Here we demonstrate doped silicon nanocrystals synthesized via a nonthermal plasma technique that exhibits tunable LSPRs in the energy range of 0.07-0.3 eV or mid-infrared wavenumbers of 600-2500 cm⁻¹.

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Journal: ACS Nano

Publication Identifier Type: DOI

Publication Identifier: 10.1021/nn400894d

Volume: 7

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Date Submitted:

Date Published:

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Article Title: Shedding Light on Vacancy-Doped Copper Chalcogenides: Shape-Controlled Synthesis, Optical Properties, and Modeling of Copper Telluride Nanocrystals with Near-Infrared Plasmon Resonances

Authors:

Keywords: copper chalcogenide nanocrystals . copper telluride nanocrystals . doped semiconductor nanocrystals . plasmon resonance . optical properties . discrete dipole approximation . Drude model . vacancy-doping

Abstract: Size- and shape-controlled synthesis of copper chalcogenide nanocrystals (NCs) is of paramount importance for a careful engineering and understanding of their optoelectronic properties and, thus, for their exploitation in energy- and plasmonic-related applications. From the copper chalcogenide family copper telluride NCs have remained fairly unexplored as a result of a poor size-, shape-, and monodispersity control that is achieved via one-step syntheses approaches. Here we show that copper telluride (namely Cu_{2-x}Te) NCs with well-defined morphologies (spheres, rods, tetrapods) can be prepared via cation exchange of preformed CdTe NCs while retaining their original shape. The resulting copper telluride NCs are characterized by pronounced plasmon bands in the near-infrared (NIR), in analogy to other copper-deficient chalcogenides (Cu_{2-x}S , Cu_{2-x}Se). We demonstrate that the extinction spectra of the as-prepared NCs are in agreement with theoretical calculations based on the discrete dipole

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Journal: The Journal of Physical Chemistry C

Publication Identifier Type: DOI

Publication Identifier: 10.1021/jp404987v

Volume: 117

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Date Submitted:

Date Published:

Publication Location:

Article Title: Optical Properties of Chiral Plasmonic Tetramers: Circular Dichroism and Multipole Effects

Authors:

Keywords: Nanoparticle clusters, plasmonic circular Dichroism, Discrete Dipole Approximation

Abstract: Chiral metal nanoparticle assemblies exhibit plasmonic circular dichroism (CD) in the visible spectral interval. It was found previously that the circular dichroism signals can be induced by dipolar interactions between nanoparticles in a chiral assembly. In order to enhance plasmonic circular dichroism response, one can take advantage of multipole effects and anisotropy of nanostructures. We calculate the plasmonic circular dichroism of several nanoparticle (NP) assemblies using the interacting point-dipole approach and the purely numerical method based on the discrete dipole approximation (DDA). We found that the multipole effects revealed by the DDA calculations are crucial to describe and understand CD responses of tightly packed assemblies. The chiral equilateral tetrahedral 4-NP complexes are especially interesting because they do not have the dipolar contribution to the CD signal. Therefore, CD signals of equilateral tetrahedral 4-NP complexes originate solely from the multipole

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Publication Identifier Type: DOI

Publication Identifier: 10.1038/ncomms3000

Volume: 4

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Date Submitted:

Date Published:

Publication Location:

Article Title: Powering the programmed nanostructure and function of gold nanoparticles with catenated DNA machines

Authors:

Keywords: Catenated DNA machines, Nanoparticle assembly,

Abstract: DNA nanotechnology is a rapidly developing research area in nanoscience. It includes the development of DNA machines, tailoring of DNA nanostructures, application of DNA nanostructures for computing, and more. Different DNA machines were reported in the past and DNA-guided assembly of nanoparticles represents an active research effort in DNA nanotechnology. Several DNA-dictated nanoparticle structures were reported, including a tetrahedron, a triangle or linear nanoengineered nanoparticle structures; however, the programmed, dynamic reversible switching of nanoparticle structures and, particularly, the dictated switchable functions emerging from the nanostructures, are missing elements in DNA nanotechnology. Here we introduce DNA catenane systems (interlocked DNA rings) as molecular DNA machines for the programmed, reversible and switchable arrangement of different-sized gold nanoparticles. We further demonstrate that the machine-powered gold nanoparticle structures reveal unique emerg

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Publication Identifier Type: DOI

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Volume: 14

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Date Submitted:

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Article Title: Fluorescence Enhancement of Molecules Inside a Gold Nanomatryoshka

Authors:

Keywords: Nanomatryoshka, fluorescence enhancement, E-field, Fano resonance, Cy7, IR800

Abstract: Metallic nanoparticles exhibiting plasmonic Fano resonances can provide large enhancements of their internal electric near field. Here we show that nanomatryoshkas, nanoparticles consisting of an Au core, an interstitial nanoscale SiO₂ layer, and an Au shell layer, can selectively provide either a strong enhancement or a quenching of the spontaneous emission of fluorophores dispersed within their internal dielectric layer. This behavior can be understood by taking into account the near-field enhancement induced by the Fano resonance of the nanomatryoshka, which is responsible for enhanced absorption of the fluorophores incorporated into the nanocomplex. The combination of compact size and enhanced light emission with internal encapsulation of the fluorophores for increased biocompatibility suggests outstanding potential for this type of nanoparticle complex in biomedical applications.

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Journal: ACSNANO

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Article Title: Using the Plasmon Linewidth To Calculate the Time and Efficiency of Electron Transfer between Gold Nanorods and Graphene

Authors:

Keywords: plasmon damping . hot electrons . one-photon photoluminescence . single-particle spectroscopy . surface plasmon resonance . graphene . plasmon linewidth

Abstract: ABSTRACT We present a quantitative analysis of the electron transfer between single gold nanorods and monolayer graphene under no electrical bias. Using single-particle dark-field scattering and photoluminescence spectroscopy to access the homogeneous linewidth, we observe broadening of the surface plasmon resonance for gold nanorods on graphene compared to nanorods on a quartz substrate. Because of the absence of spectral plasmon shifts, dielectric interactions between the gold nanorods and graphene are not important and we instead assign the plasmon damping to charge transfer between plasmon-generated hot electrons and the graphene that acts as an efficient acceptor. Analysis of the plasmon linewidth yields an average electron transfer time of 160 (30 fs, which is otherwise difficult to measure directly in the time domain with single-particle sensitivity. In comparison to intrinsic hot electron decay and radiative relaxation, we furthermore calculate from the plasmon linewidth that

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Publication Identifier Type: DOI

Publication Identifier: 10.1038/ncomms4299

Volume: 5

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Date Submitted:

Date Published:

Publication Location:

Article Title: Optophotonics with coupled quantum dots

Authors:

Keywords: Physical sciences• Condensed matter• Optical physics

Abstract: technology is founded on the intimate understanding of how to utilize and control electrons. Next to electrons, nature uses phonons, quantized vibrations of an elastic structure, to carry energy, momentum and even information through solids. Phonons permeate the crystalline components of modern technology, yet in terms of technological utilization phonons are far from being on par with electrons. Here we demonstrate how phonons can be employed to render a single quantum dot pair optically transparent. This phonon-induced transparency is realized via the formation of a molecular polaron, the result of a Fano-type quantum interference, which proves that we have accomplished making typically incoherent and dissipative phonons behave in a coherent and non-dissipative manner. We find the transparency to be widely tunable by electronic and optical means. Thereby we show amplification of weakest coupling channels. We further outline the molecular polaron's potential as a control element in ph

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Article Title: Orienting Nanoantennas in Three Dimensions To Control Light Scattering Across a Dielectric Interface

Authors:

Keywords: Plasmon; nanoparticles; nanocup; nanoshell; nanoantenna; symmetry breaking; scattering; dielectric interface; total internal reflection

Abstract: The light scattering properties of hemispherical resonant nanoantennas can be used to redirect normal incidence light to propagate within a thin film or thin film-based device, such as a solar cell, for enhanced efficiency. While planar nanoantennas are typically fabricated as simple nanoparticles or nanostructures in the film plane, here we show that a hemispherical nanoantenna with its symmetry axis tilted out of the plane accomplishes this task with far greater efficacy. The amount of light scattered into an underlying dielectric by the electric and magnetic dipole response of oriented nanocups can be more than three times that achieved using symmetric antenna structures.

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Journal: ACSNANO

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Volume: 8

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Date Submitted:

Date Published:

Publication Location:

Article Title: Aluminum for plasmonics.

Authors:

Keywords: plasmon; UV; dark field; hyperspectral; nanodisk; aluminum

Abstract: Unlike silver and gold, aluminum has material properties that enable strong plasmon resonances spanning much of the visible region of the spectrum and into the ultraviolet. This extended response, combined with its natural abundance, low cost, and amenability to manufacturing processes, makes aluminum a highly promising material for commercial applications. Fabricating Al-based nanostructures whose optical properties correspond with theoretical predictions, however, can be a challenge. In this work, the Al plasmon resonance is observed to be remarkably sensitive to the presence of oxide within the metal. For Al nanodisks, we observe that the energy of the plasmon resonance is determined by, and serves as an optical reporter of, the percentage of oxide present within the Al. This understanding paves the way toward the use of aluminum as a low-cost plasmonic material with properties and potential applications similar to those of the coinage metals.

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Date Submitted:

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Article Title: Cation exchange synthesis and optoelectronic properties of type II CdTe–Cu₂xTe nano-heterostructures

Authors:

Keywords: Cation exchange synthesis and optoelectronic properties of type II CdTe–Cu₂xTe nano-heterostructures

Abstract: Rod-shaped CdTe–Cu₂xTe nano-heterostructures with tunable dimensions of both sub-units and a type II band alignment were prepared by Cd²⁺/Cu⁺ cation exchange. The light absorption properties of the heterostructures are dominated by the excitonic and plasmonic contributions arising, respectively, from the CdTe and the Cu₂xTe sub-units. These results were confirmed over a wide range of sub-unit length fractions through optical modelling based on the discrete dipole approximation (DDA). Although assuming electronically independent sub-units, our modelling results indicate a negligible ground state interaction between the CdTe exciton and the Cu₂xTe plasmon. This lack of interaction may be due to the low spectral overlap between exciton and plasmon, but also to localization effects in the vacancy-doped sub-unit. The electronic interaction between both sub-units was evaluated with pump-probe spectroscopy by assessing the relaxation dynamics of the excitonic transition. In particular, the

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Date Submitted:

Date Published:

Publication Location:

Article Title: Quantum Plasmonics: Optical Properties of a Nanomatrushka

Authors:

Keywords: Time-dependent density functional theory (TDDFT), localized surface plasmon resonance (LSPR), quantum plasmonics

Abstract: Quantum mechanical effects can significantly reduce the plasmon-induced field enhancements around nanoparticles. Here we present a quantum mechanical investigation of the plasmon resonances in a nanomatrushka, which is a concentric core-shell nanoparticle consisting of a solid metallic core encapsulated in a thin metallic shell. We compute the optical response using the time-dependent density functional theory and compare the results with predictions based on the classical electromagnetic theory. We find strong quantum mechanical effects for core-shell spacings below 5 Å, a regime where both the absorption cross section and the local field enhancements differ significantly from the classical predictions. We also show that the workfunction of the metal is a crucial parameter determining the onset and magnitude of quantum effects. For metals with lower workfunctions such as aluminum, the quantum effects are found to be significantly more pronounced than for a noble metal such as gold.

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Journal: ACSNANO

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Volume: 8

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Date Submitted:

Date Published:

Publication Location:

Article Title: Influence of Cross Sectional Geometry on Surface Plasmon Polariton Propagation in Gold Nanowires

Authors:

Keywords: gold nanowires . surface plasmon polaritons . plasmon propagation . plasmonic waveguides . cross sectional geometry

Abstract: We investigated the effects of cross sectional geometry on surface plasmon polariton propagation in gold nanowires (NWs) using bleach-imaged plasmon propagation and electromagnetic simulations. Chemically synthesized NWs have pentagonally twinned crystal structures, but recent advances in synthesis have made it possible to amplify this pentagonal shape to yield NWs with a five-pointed-star cross section and sharp end tips. We found experimentally that NWs with a five-pointed-star cross section, referred to as SNWs, had a shorter propagation length for surface plasmon polaritons at 785 nm, but a higher effective incoupling efficiency compared to smooth NWs with a pentagonal cross section, labeled as PNWs. Electromagnetic simulations revealed that the electric fields were localized at the sharp ridges of the SNWs, leading to higher absorptive losses and hence shorter propagation lengths compared to PNWs. On the other hand, scattering losses were found to be relatively uncorrelated with c

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Journal: Nano Letters

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Date Submitted:

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Article Title: Dye-Assisted Gain of Strongly Confined Surface Plasmon Polaritons in Silver Nanowires

Authors:

Keywords: Surface plasmons; silver nanowires; plasmonic waveguides; loss compensation; gain

Abstract: Noble metal nanowires are excellent candidates as subwavelength optical components in miniaturized devices due to their ability to support the propagation of surface plasmon polaritons (SPPs). Nanoscale data transfer based on SPP propagation at optical frequencies has the advantage of larger bandwidths but also suffers from larger losses due to strong mode confinement. To overcome losses, SPP gain has been realized, but so far only for weakly confined SPPs in metal films and stripes. Here we report the demonstration of gain for subwavelength SPPs that were strongly confined in chemically prepared silver nanowires (mode area = $\lambda^2/40$) using a dye-doped polymer film as the optical gain medium. Under continuous wave excitation at 514 nm, we measured a gain coefficient of 270 cm^{-1} for SPPs at 633 nm, resulting in partial SPP loss compensation of 14%. This achievement for strongly confined SPPs represents a major step forward toward the realization of nanoscale plasmonic amplifiers and laser

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Volume: 4

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Date Submitted:

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Publication Location:

Article Title: Chiral plasmonic DNA nanostructures with switchable circular dichroism

Authors:

Keywords: No keywords

Abstract: Circular dichroism spectra of naturally occurring molecules and also of synthetic chiral arrangements of plasmonic particles often exhibit characteristic bisignate shapes. Such spectra consist of peaks next to dips (or vice versa) and result from the superposition of signals originating from many individual chiral objects oriented randomly in solution. Here we show that by first aligning and then toggling the orientation of DNA-origami-scaffolded nanoparticle helices attached to a substrate, we are able to reversibly switch the optical response between two distinct circular dichroism spectra corresponding to either perpendicular or parallel helix orientation with respect to the light beam. The observed directional circular dichroism of our switchable plasmonic material is in good agreement with predictions based on dipole approximation theory. Such dynamic metamaterials introduce functionality into soft matter-based optical devices and may enable novel data storage schemes or signal mo

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Article Title: Quantum Plasmonics: Optical Properties of a NanomatryushkaACS ActiveView PDFHi-Res Print, Annotate, Reference QuickViewPDF [1563 KB]PDF w/ Links[336 KB]Full Text HTMLAbstractSupporting Info - >PDFnI402662e_si_001.pdf (334.32 kb)FiguresReference QuickViewCiting ArticlesAdd to ACS ChemWorx Vikram Kulkarni †, Emil Prodan ‡, and Peter

Authors:

Keywords: Time-dependent density functional theory (TDDFT), localized surface plasmon resonance (LSPR), quantum plasmonics

Abstract: Quantum mechanical effects can significantly reduce the plasmon-induced field enhancements around nanoparticles. Here we present a quantum mechanical investigation of the plasmon resonances in a nanomatryushka, which is a concentric core-shell nanoparticle consisting of a solid metallic core encapsulated in a thin metallic shell. We compute the optical response using the time-dependent density functional theory and compare the results with predictions based on the classical electromagnetic theory. We find strong quantum mechanical effects for core-shell spacings below 5 Å, a regime where both the absorption cross section and the local field enhancements differ significantly from the classical predictions. We also show that the workfunction of the metal is a crucial parameter determining the onset and magnitude of quantum effects. For metals with lower workfunctions such as aluminum, the quantum effects are found to be significantly more pronounced than for a noble metal such as gold.

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Journal: Nanoscale
Publication Identifier Type: **Publication Identifier:**
Volume: 6 **Issue:** 4 **First Page #:** 2077
Date Submitted: **Date Published:**
Publication Location:
Article Title: 3D plasmonic chiral colloids.
Authors:
Keywords: To Be Determined
Abstract: 3D plasmonic chiral colloids are synthesized through deterministically grouping of two gold nanorod AuNRs on DNA origami. These nanorod crosses exhibit strong circular dichroism (CD) at optical frequencies which can be engineered through position tuning of the rods on the origami. Our experimental results agree qualitatively well with theoretical predictions.
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Journal: Nano Letters
Publication Identifier Type: **Publication Identifier:**
Volume: 0 **Issue:** 0 **First Page #:** 4399
Date Submitted: **Date Published:**
Publication Location:
Article Title: Three-Dimensional Plasmonic Nanoclusters
Authors:
Keywords: Plasmonics, dark-field spectroscopy, metamolecule, metafluid, nanoclusters
Abstract: Assembling nanoparticles into well-defined structures is an important way to create and tailor the optical properties of materials. Most advances in metamaterials research to date have been based on structures fabricated in two-dimensional planar geometries. Here, we show an efficient method for assembling noble metal nanoparticles into stable, three-dimensional (3-D) clusters, whose optical properties can be highly sensitive or remarkably independent of cluster orientation, depending on particle number and cluster geometry. Some of the clusters, such as tetrahedra and icosahedra, could serve as the optical kernels for metafluids, imparting metamaterial optical properties into disordered media such as liquids, glasses, or plastics, free from the requirement of nanostructure orientation.
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Date Submitted:

Date Published:

Publication Location:

Article Title: Chiral Plasmonic Nanostructures on Achiral Nanopillars

Authors:

Keywords: Chirality, plasmonic chirality, ZnO, nanopillars, circular dichroism, three-dimensional thin films, 3D chirality

Abstract: Chirality of plasmonic films can be strongly enhanced by threedimensional (3D) out-of-plane geometries. The complexity of lithographic methods currently used to produce such structures and other methods utilizing chiral templates impose limitations on spectral windows of chiroptical effects, the size of substrates, and hence, further research on chiral plasmonics. Here we demonstrate 3D chiral plasmonic nanostructures (CPNs) with high optical activity in the visible spectral range based on initially achiral nanopillars from ZnO. We made asymmetric gold nanoshells on the nanopillars by vacuum evaporation at different inclination and rotation angles to achieve controlled symmetry breaking and obtained both left- and rightrotating isomers. The attribution of chiral optical effects to monolithic enantiomers made in this process was confirmed by theoretical calculations based on their geometry established from scanning electron microscope (SEM) images. The chirality of the nanoshells is ret

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Journal: The Journal of Physical Chemistry C

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Volume: 118

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Date Submitted:

Date Published:

Publication Location:

Article Title: Theory of Quantum Plasmon Resonances in Doped SemiconductorNanocrystals

Authors:

Keywords: To be Determined

Abstract: Doped semiconductor nanocrystals represent a new type of quantum plasmonic material with optical resonances in the infrared. These nanocrystals are fundamentally different from the metal nanoparticles because the electron density in a semiconductor can be tuned over a wide interval. Using the DFT-based time-dependent formalism, we computed the absorption spectra of doped quantum dots as a function of the number of carriers in the dot. The dynamic properties of doped quantum dots undergo an interesting transition from the size-quantization regime to the classical regime of plasmon oscillations. We demonstrated this quantum-to-classical transition for both self-doped copper chalcogenide dots and impurity-doped II?VI nanocrystals. We also showed that the plasmon frequency and electron density in the dot depend on the type of doping, which can be bulk-like or surface-like. The results obtained in this study can be used to predict and describe optical properties of a variety of semiconducto

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Journal: Advanced Functional Materials

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Volume: 24

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Date Submitted:

Date Published:

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Article Title: Self-Assembly Mechanism of Spiky Magnetoplasmonic Supraparticles

Authors:

Keywords: To Be Determined

Abstract: Concave nanoparticles (NPs) with complex angled and non-Platonic geometries have unique optical, magnetic, catalytic, and biological properties originating from the singularities of the electrical field in apexes and craters. Preparation of such particles with a uniform size/shape and core-shell morphology represents a significant challenge, largely because of the poor knowledge of their formation mechanism. Here, this challenge is addressed and a study of the mechanism of their formation is presented for a case of complex spiky morphologies that led us to the conclusion that NPs with concave geometries can be, in fact, supraparticles (SPs) produced via the self-assembly of smaller convex integrants. This mechanism is exemplified by the vivid case of spiky SPs formed via the attachment of small and faceted Au NPs on smooth Au-coated iron oxide (Fe_3O_4 @Au) seeds. The theoretical calculations of energies of primary interactions—electrostatic repulsion and van-der Waals repulsion, e

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Journal: Nano Letters

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Date Submitted:

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Article Title: Turning the Corner: Efficient Energy Transfer in Bent Plasmonic Nanoparticle Chain Waveguides

Authors:

Keywords: Surface plasmon resonance, surface plasmon polariton, plasmon waveguiding, super- and subradiant modes, BIIPP, silver nanoparticle

Abstract: For integrating and multiplexing of subwavelength plasmonic waveguides with other optical and electric components, complex architectures such as junctions with sharp turns are necessary. However, in addition to intrinsic losses, bending losses severely limit plasmon propagation. In the current work, we demonstrate that propagation of surface plasmon polaritons around 90° turns in silver nanoparticle chains occurs without bending losses. Using a far-field fluorescence method, bleach-imaged plasmon propagation (BIIPP), which creates a permanent map of the plasmonic near-field through bleaching of a fluorophore coated on top of a plasmonic waveguide, we measured propagation lengths at 633 nm for straight and bent silver nanoparticle chains of 8.0 ± 0.5 and $7.8 \pm 0.4 \mu\text{m}$, respectively. These propagation lengths were independent of the input polarization. We furthermore show that subradiant plasmon modes yield a longer propagation length compared to energy transport via excitation of super-r

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Date Submitted:

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Article Title: Unexpected Chirality of Nanoparticle Dimers and Ultrasensitive Chiroplasmonic Bioanalysis

Authors:

Keywords: To Be Determined

Abstract: Chiral assemblies of nanoparticles (NPs) are typically constructed with helical or tetrahedral geometries. Simple pairs of NPs are not expected to display chirality due to basic symmetry considerations made under the assumption of their spherical geometry. In this study we demonstrate that assemblies consisting of two metallic NPs do possess chirality and strongly rotate polarization of light. Their chiroplasmonic properties are attributed to the prolate geometry of individual colloidal particles. When bridged by biomolecules, the NP pairs acquire scissor-like geometry, with the long axes of NPs forming an angle of $\sim 9^\circ$. This small dihedral angle results in chirality of the NP pair, while the consistency of its sign due to the specific conformation of the bridging biomacromolecules breaks the enantiomeric equivalence of the NP pairs. Strong polarization rotation in these nanoassemblies makes possible their utilization in biological analysis. Heterodimers of gold and silver NPs were made

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Volume: 8

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Date Submitted:

Date Published:

Publication Location:

Article Title: Controlled Doping of Silicon Nanocrystals Investigated by Solution-Processed Field Effect Transistors

Authors:

Keywords: Silicon, Nanocrystals, field effect transistor . dopants . phosphorus . boron

Abstract: The doping of semiconductor nanocrystals (NCs), which is vital for the optimization of NC-based devices, remains a significant challenge. While gas-phase plasma approaches have been successful in incorporating dopant atoms into NCs, little is known about their electronic activation. Here, we investigate the electronic properties of doped silicon NC thin films cast from solution by field effect transistor analysis. We find that, analogous to bulk silicon, boron and phosphorus electronically dope Si NC thin films; however, the dopant activation efficiency is only $\sim 10^{-2}$ to 10^{-4} . We also show that surface doping of Si NCs is an effective way to alter the carrier concentrations in Si NC films.

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Date Submitted:

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Article Title: Self-Assembly of Copper Sulfide Nanoparticles into Nanoribbons with Continuous Crystallinity

Authors:

Keywords: nanoparticles . copper sulfide, aqueous dispersions . nanoribbons

Abstract: Copper chalcogenide nanoparticles (NPs) represent a promising material for solar energy conversion, electrical charge storage, and plasmonic devices. However, it is difficult to achieve highquality NP dispersions in experimentally convenient and technologically preferred aqueous media. Also problematic is the transition from NP dispersion to continuously crystalline nanoscale materials, for instance, nanowires, nanoribbons, or similar high aspect ratio nano/microstructures capable of charge transport necessary for such applications. All previous examples of copper sulfide assemblies contained insulating gaps between NPs. Here we show that aqueous synthesis of high-quality monodispersed high-chalcocite γ -Cu₂S NPs, with sizes from 2 to 10 nm, is possible. When reaction time increased, the NP shape evolved from nearly spherical particles into disks with predominantly hexagonal shape. Moreover, the monodispersed γ -Cu₂S NPs were found to spontaneously self-assemble into nanochains and, subs

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Date Submitted:

Date Published:

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Article Title: Self-Assembly Mechanism of Spiky Magnetoplasmonic Supraparticles

Authors:

Keywords: Iron Oxide Nanoparticles, Seeded growth, Spiky nanoparticles

Abstract: Concave nanoparticles (NPs) with complex angled and non-Platonic geometries have unique optical, magnetic, catalytic, and biological properties originating from the singularities of the electrical field in apexes and craters. Preparation of such particles with a uniform size/shape and core-shell morphology represents a significant challenge, largely because of the poor knowledge of their formation mechanism. Here, this challenge is addressed and a study of the mechanism of their formation is presented for a case of complex spiky morphologies that led us to the conclusion that NPs with concave geometries can be, in fact, supraparticles (SPs) produced via the self-assembly of smaller convex integrants. This mechanism is exemplified by the vivid case of spiky SPs formed via the attachment of small and faceted Au NPs on smooth Au-coated iron oxide (Fe₃O₄@Au) seeds. The theoretical calculations of energies of primary interactions—electrostatic repulsion and van-der Waals repulsion, e

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Date Submitted:

Date Published:

Publication Location:

Article Title: Aluminum for Plasmonics

Authors:

Keywords: plasmon . UV . dark field . hyperspectral . nanodisk . aluminum

Abstract: Unlike silver and gold, aluminum has material properties that enable strong plasmon resonances spanning much of the visible region of the spectrum and into the ultraviolet. This extended response, combined with its natural abundance, low cost, and amenability to manufacturing processes, makes aluminum a highly promising material for commercial applications. Fabricating Al-based nanostructures whose optical properties correspond with theoretical predictions, however, can be a challenge. In this work, the Al plasmon resonance is observed to be remarkably sensitive to the presence of oxide within the metal. For Al nanodisks, we observe that the energy of the plasmon resonance is determined by, and serves as an optical reporter of, the percentage of oxide present within the Al. This understanding paves the way toward the use of aluminum as a low-cost plasmonic material with properties and potential applications similar to those of the coinage metals.

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Volume: 118

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Date Submitted:

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Publication Location:

Article Title: Impurity-Induced Plasmon Damping in Individual Cobalt-Doped Hollow Au Nanoshells

Authors:

Keywords: cobalt core, hollow nanoshells, FWHM broadening, TIRS

Abstract: The optical properties of plasmonic nanoparticles in the size range corresponding to the electrostatic, or dipole, limit have the potential to reveal effects otherwise masked by phase retardation. Here we examine the optical properties of individual, sub-50 nm hollow Au nanoshells (Co-HGNS), where Co is the initial sacrificial core nanoparticle, using single particle total internal reflection scattering (TIRS) spectroscopy. The residual Co present in the metallic shell induces a substantial broadening of the homogeneous plasmon resonance line width of the CoHGNS, where the full width at half-maximum (fwhm) broadens proportionately with increasing Co content. This doping-induced line broadening provides a strategy for controlling plasmon line width independent of nanoparticle size, and has the potential to substantially modify the relative decay channels for localized nanoparticle surface plasmons.

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Volume: 118

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Date Submitted:

Date Published:

Publication Location:

Article Title: Theory of Quantum Plasmon Resonances in Doped Semiconductor Nanocrystals

Authors:

Keywords: Semiconductor Nanocrystal, DFT, quantum plasmonics

Abstract: Doped semiconductor nanocrystals represent a new type of quantum plasmonic material with optical resonances in the infrared. These nanocrystals are fundamentally different from the metal nanoparticles because the electron density in a semiconductor can be tuned over a wide interval. Using the DFT-based time-dependent formalism, we computed the absorption spectra of doped quantum dots as a function of the number of carriers in the dot. The dynamic properties of doped quantum dots undergo an interesting transition from the size-quantization regime to the classical regime of plasmon oscillations. We demonstrated this quantum-to-classical transition for both self-doped copper chalcogenide dots and impurity-doped II-VI nanocrystals. We also showed that the plasmon frequency and electron density in the dot depend on the type of doping, which can be bulk-like or surface-like. The results obtained in this study can be used to predict and describe optical properties of a variety of semiconductors.

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Date Published:

Publication Location:

Article Title: Shell-Engineered Chiroplasmonic Assemblies of Nanoparticles for Zeptomolar DNA Detection

Authors:

Keywords: Nanoparticle assemblies, chiroplasmonic properties, core-shell deposition, amplification, biosensing

Abstract: DNA-bridged pairs of seemingly spherical metallic nanoparticles (NPs) have chiral geometry due to the nonideal oblong shape of the particles and scissor-like conformation. Here we demonstrate that deposition of gold and silver shells around the NP heterodimers enables spectral modulation of their chiroplasmonic bands in 400–600 nm region and results in significantly enhanced optical activity with g-factors reaching 1.21×10^2 . The multimetal heterodimers optimized for coupling with the spin angular momentum of incident photons enable polymerase chain reaction (PCR)-based DNA detection at the zeptomolar level. This significant improvement in the sensitivity of detection is attributed to improvement of base pairing in the presence of NPs, low background for chiroplasmonic detection protocol, and enhancement of photon-plasmon coupling for light with helicity matching that of the twisted geometry of the heterodimers.

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Article Title: Plasmonic Metamaterials and Nanocomposites with the Narrow Transparency Window Effect in Broad Extinction Spectra

Authors:

Keywords: metamaterial, optical properties, transparency, plasmon, nanocomposite, nanorod, nanowire

Abstract: We propose and describe plasmonic nanomaterials with unique optical properties. These nanostructured materials strongly attenuate light across a broad wavelength interval ranged from 400 nm to 5 μ m but exhibit a narrow transparency window centered at a given wavelength. The main elements used in our systems are nanorods and nanocrosses of variable sizes. The nanomaterial can be designed as a solution, nanocomposite film or metastructure. The principle of the formation of the transparency window in the broad extinction spectrum is based on the narrow lines of longitudinal plasmons of single nanorods and nanorod complexes. To realize the spectrum with a transmission window, we design a nanocomposite material as a mixture of nanorods of different sizes. Simultaneously, we exclude nanorods of certain lengths from the nanorod ensemble. The width of the plasmonic transparency window is determined by the intrinsic and radiative broadenings of the nanocrystal plasmons. Nanocrystals can be random

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Journal: Nature Materials

Publication Identifier Type: DOI

Publication Identifier: 10.1038/nmat4125

Volume: 14

Issue: 1

First Page #: 66

Date Submitted:

Date Published:

Publication Location:

Article Title: Chiral templating of self-assembling nanostructures by circularly polarized light

Authors:

Keywords: CdTe Nanoparticles, chirality,

Abstract: The high optical and chemical activity of nanoparticles (NPs) signifies the possibility of converting the spin angular momenta of photons into structural changes in matter. Here, we demonstrate that illumination of dispersions of racemic CdTe NPs with right- (left-)handed circularly polarized light (CPL) induces the formation of right- (left-)handed twisted nanoribbons with an enantiomeric excess exceeding 30%, which is ~ 10 times higher than that of typical CPL-induced reactions. Linearly polarized light or dark conditions led instead to straight nanoribbons. CPL 'templating' of NP assemblies is based on the enantio-selective photoactivation of chiral NPs and clusters, followed by their photooxidation and self-assembly into nanoribbons with specific helicity as a result of chirality-sensitive interactions between the NPs. The ability of NPs to retain the polarization information of incident photons should open pathways for the synthesis of chiral photonic materials and allow a better understanding

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Journal: Chem Soc Review
Publication Identifier Type: DOI **Publication Identifier:** 10.1039/C4CS00131A
Volume: 44 **Issue:** 1 **First Page #:** 40
Date Submitted: **Date Published:**
Publication Location:

Article Title: Optical characterization of single plasmonic nanoparticles

Authors:

Keywords: single particle spectroscopy, Mie and Gans theory, super-resolution fluorescence microscopy.

Abstract: This tutorial review surveys the optical properties of plasmonic nanoparticles studied by various single particle spectroscopy techniques. The surface plasmon resonance of metallic nanoparticles depends sensitively on the nanoparticle geometry and its environment, with even relatively minor deviations causing significant changes in the optical spectrum. Because for chemically prepared nanoparticles a distribution of their size and shape is inherent, ensemble spectra of such samples are inhomogeneously broadened, hiding the properties of the individual nanoparticles. The ability to measure one nanoparticle at a time using single particle spectroscopy can overcome this limitation. This review provides an overview of different steady-state single particle spectroscopy techniques that provide detailed insight into the spectral characteristics of plasmonic nanoparticles.

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI **Publication Identifier:** 10.1021/ja4095445
Volume: 135 **Issue:** 49 **First Page #:** 18629
Date Submitted: **Date Published:**
Publication Location:

Article Title: Unexpected Chirality of Nanoparticle Dimers and Ultrasensitive Chiroplasmonic Bioanalysis

Authors:

Keywords: Chiral nanoparticle dimers

Abstract: Chiral assemblies of nanoparticles (NPs) are typically constructed with helical or tetrahedral geometries. Simple pairs of NPs are not expected to display chirality due to basic symmetry considerations made under the assumption of their spherical geometry. In this study we demonstrate that assemblies consisting of two metallic NPs do possess chirality and strongly rotate polarization of light. Their chiroplasmonic properties are attributed to the prolate geometry of individual colloidal particles. When bridged by biomolecules, the NP pairs acquire scissor-like geometry, with the long axes of NPs forming an angle of $\sim 9^\circ$. This small dihedral angle results in chirality of the NP pair, while the consistency of its sign due to the specific conformation of the bridging biomacromolecules breaks the enantiomeric equivalence of the NP pairs. Strong polarization rotation in these nanoassemblies makes possible their utilization in biological analysis. Heterodimers of gold and silver NPs were made

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Journal: ACS Nano

Publication Identifier Type: DOI

Publication Identifier: 10.1021/nn404985h

Volume: 7

Issue: 12

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Date Submitted:

Date Published:

Publication Location:

Article Title: Using the Plasmon Linewidth To Calculate the Time and Efficiency of Electron Transfer between Gold Nanorods and Graphene

Authors:

Keywords: plasmon damping . hot electrons . one-photon photoluminescence . single-particle spectroscopy . surface plasmon resonance . graphene . plasmon linewidth

Abstract: We present a quantitative analysis of the electron transfer between single gold nanorods and monolayer graphene under no electrical bias. Using single-particle dark-field scattering and photoluminescence spectroscopy to access the homogeneous linewidth, we observe broadening of the surface plasmon resonance for gold nanorods on graphene compared to nanorods on a quartz substrate. Because of the absence of spectral plasmon shifts, dielectric interactions between the gold nanorods and graphene are not important and we instead assign the plasmon damping to charge transfer between plasmon-generated hot electrons and the graphene that acts as an efficient acceptor. Analysis of the plasmon linewidth yields an average electron transfer time of 160 (30 fs, which is otherwise difficult to measure directly in the time domain with single-particle sensitivity. In comparison to intrinsic hot electron decay and radiative relaxation, we furthermore calculate from the plasmon linewidth that charge tr

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Journal: ACS Nano

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Publication Identifier: 10.1021/acs.nano.5b02087

Volume: 9.0E+000 Issue: 6.0E+000 First Page #: 6428

Date Submitted:

Date Published:

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Article Title: Charge Transfer Plasmons: Optical Frequency Conductances and Tunable Infrared Resonances

Authors:

Keywords: charge transfer plasmon . optical antenna . IR plasmon . electric current . single-particle dark-field spectroscopy . electron beam lithography

Abstract: A charge transfer plasmon (CTP) appears when an optical-frequency conductive pathway between two metallic nanoparticles is established, enabling the transfer of charge between nanoparticles when the plasmon is excited. Here we investigate the properties of the CTP in a nanowire-bridged dimer geometry. Varying the junction geometry controls its conductance, which modifies the resonance energies and scattering intensities of the CTP while also altering the other plasmon modes of the nanostructure. Reducing the junction conductance shifts this resonance to substantially lower energies in the near- and mid-infrared regions of the spectrum. The CTP offers both a high-information probe of optical frequency conductances in nanoscale junctions and a new, unique approach to controllably engineering tunable plasmon modes at infrared wavelengths.

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Journal: Nano Letters

Publication Identifier Type: DOI

Publication Identifier: 10.1021/acs.nanolett.5b00614

Volume: 1.5E+001 Issue: 4.0E+000 First Page #: 2751

Date Submitted:

Date Published:

Publication Location:

Article Title: Aluminum Nanocrystals

Authors:

Keywords: aluminum nanocrystals, synthesis, plasmon

Abstract: We demonstrate the facile synthesis of high purity aluminum nanocrystals over a range of controlled sizes from 70 to 220 nm diameter with size control achieved through a simple modification of solvent ratios in the reaction solution. The monodisperse, icosahedral, and trigonal bipyramidal nanocrystals are air-stable for weeks, due to the formation of a 2–4 nm thick passivating oxide layer on their surfaces. We show that the nanocrystals support size-dependent ultraviolet and visible plasmon modes, providing a far more sustainable alternative to gold and silver nanoparticles currently in widespread use.

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Journal: ACS Nano

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Publication Identifier: 10.1021/acsnano.5b00412

Volume: 9.0E+000 Issue: 3.0E+000 First Page #: 3284

Date Submitted:

Date Published:

Publication Location:

Article Title: Fractal Nanoparticle Plasmonics: The Cayley Tree

Authors:

Keywords: plasmons; fractal; Cayley tree; nanoantenna

Abstract: There has been strong, ongoing interest over the past decade in developing strategies to design and engineer materials with tailored optical properties. Fractal-like nanoparticles and films have long been known to possess a remarkably broad-band optical response and are potential nanoscale components for realizing spectrum-spanning optical effects. Here we examine the role of self-similarity in a fractal geometry for the design of plasmon line shapes. By computing and fabricating simple Cayley tree nanostructures of increasing fractal order N , we are able to identify the principle behind how the multimodal plasmon spectrum of this system develops as the fractal order is increased. With increasing N , the fractal structure acquires an increasing number of modes with certain degeneracies: these modes correspond to plasmon oscillations on the different length scales inside a fractal. As a result, fractals with large N exhibit broad, multi-peaked spectra from plasmons with large degeneracy n

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Journal: Nature Communications
Publication Identifier Type: DOI **Publication Identifier:** 10.1038/ncomms8022
Volume: 6.0E+000 **Issue:** 0 **First Page #:** 7022
Date Submitted: **Date Published:**
Publication Location:

Article Title: Tuning the acoustic frequency of a gold nanodisk through its adhesion layer

Authors:

Keywords: gold nanodisk, acoustic frequency,

Abstract: To fabricate robust metallic nanostructures with top-down patterning methods such as electron-beam lithography, an initial nanometer-scale layer of a second metal is deposited to promote adhesion of the metal of interest. However, how this nanoscale layer affects the mechanical properties of the nanostructure and how adhesion layer thickness controls the binding strength to the substrate are still open questions. Here we use ultrafast laser pulses to impulsively launch acoustic phonons in single gold nanodisks with variable titanium layer thicknesses, and observe an increase in phonon frequencies as a thicker adhesion layer facilitates stronger binding to the glass substrate. In addition to an all-optical interrogation of nanoscale mechanical properties, our results show that the adhesion layer can be used to controllably modify the acoustic phonon modes of a gold nanodisk. This direct coupling between optically excited plasmon modes and phonon modes can be exploited for a variety of e

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Journal: ACS Nano
Publication Identifier Type: DOI **Publication Identifier:** 10.1021/acsnano.5b03090
Volume: 0 **Issue:** 0 **First Page #:** 0
Date Submitted: **Date Published:**
Publication Location:

Article Title: High-Density 2D Homo- and Hetero- Plasmonic Dimers with Universal Sub-10-nm Gaps

Authors:

Keywords: plasmonic dimers, nanoimprint lithography, shadow evaporation, EELS, FDTD, plasmon hybridization

Abstract: Fabrication of high-density plasmonic dimers on a large (wafer) scale is crucial for applications in surface-enhanced spectroscopy, bio- and molecular sensing, and optoelectronics. Here, we present an experimental approach based on nanoimprint lithography and shadow evaporation that allows for the fabrication of high-density, large-scale homo- (Au/Au and Ag/Ag) and hetero- (Au/Ag) dimer substrates with precise and consistent sub-10-nm gaps. We performed scanning electron, scanning transmission electron, and atomic force microscopy studies along with a complete electron energy-loss spectroscopy (EELS) characterization. We observed distinct plasmonic modes on these dimers, which are well interpreted by finite-difference time-domain (FDTD) and plasmon hybridization calculations.

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Journal: Nano Letters

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Publication Identifier: 10.1021/nl504992h

Volume: 1.5E+001 Issue: 5.0E+000 First Page #: 3041

Date Submitted:

Date Published:

Publication Location:

Article Title: Single-Particle Absorption Spectroscopy by Photothermal Contrast

Authors:

Keywords: Single-particle spectroscopy, absorption spectroscopy, photothermal imaging, gold nanoparticle, gold nanorod, surface plasmon

Abstract: Removing effects of sample heterogeneity through single-molecule and single-particle techniques has advanced many fields. While background free luminescence and scattering spectroscopy is widely used, recording the absorption spectrum only is rather difficult. Here we present an approach capable of recording pure absorption spectra of individual nanostructures. We demonstrate the implementation of single-particle absorption spectroscopy on strongly scattering plasmonic nanoparticles by combining photothermal microscopy with a supercontinuum laser and an innovative calibration procedure that accounts for chromatic aberrations and wavelength-dependent excitation powers. Comparison of the absorption spectra to the scattering spectra of the same individual gold nanoparticles reveals the blueshift of the absorption spectra, as predicted by Mie theory but previously not detectable in extinction measurements that measure the sum of absorption and scattering. By covering a wavelength range of

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Journal: Nature Nanotechnology

Publication Identifier Type: DOI

Publication Identifier: 10.1038/nnano.2015.165

Volume: 0 Issue: 0 First Page #: 0

Date Submitted:

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Publication Location:

Article Title: Anomalous ultrafast dynamics of hot plasmonic electrons in nanostructures with hot spots

Authors:

Keywords: gold nanodisks, ultrafast dynamics

Abstract: The interaction of light and matter in metallic nanosystems is mediated by the collective oscillation of surface electrons, called plasmons¹. After excitation, plasmons are absorbed by the metal electrons through inter- and intraband transitions, creating a highly non-thermal distribution of electrons^{2–4}. The electron population then decays through electron–electron interactions, creating a hot electron distribution within a few hundred femtoseconds, followed by a further relaxation via electron–phonon scattering on the timescale of a few picoseconds^{5–8}. In the spectral domain, hot plasmonic electrons induce changes to the plasmonic resonance of the nanostructure by modifying the dielectric constant of the metal^{5,9}. Here, we report on the observation of anomalously strong changes to the ultrafast temporal and spectral responses of these excited hot plasmonic electrons in hybrid metal/oxide nanostructures as a result of varying the geometry and composition of the nanostructure and the

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Publication Identifier: 10.1038/nature14092

Volume: 5.17E+002 Issue: 7.536E+00 First Page #: 596

Date Submitted:

Date Published:

Publication Location:

Article Title: Anomalous dispersions of 'hedgehog' particles

Authors:

Keywords: Synthesis and processing, Colloids, Wetting

Abstract: Hydrophobic particles in water and hydrophilic particles in oil aggregate, but can form colloidal dispersions if their surfaces are chemically camouflaged with surfactants, organic tethers, adsorbed polymers or other particles that impart affinity for the solvent and increase interparticle repulsion^{1, 2}. A different strategy for modulating the interaction between a solid and a liquid uses surface corrugation, which gives rise to unique wetting behaviour^{3, 4, 5}. Here we show that this topographical effect can also be used to disperse particles in a wide range of solvents without recourse to chemicals to camouflage the particles' surfaces: we produce micrometre-sized particles that are coated with stiff, nanoscale spikes and exhibit long-term colloidal stability in both hydrophilic and hydrophobic media. We find that these 'hedgehog' particles do not interpenetrate each other with their spikes, which markedly decreases the contact area between the particles and, therefore, the attractive

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Journal: Nano Letters

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Publication Identifier: 10.1021/acs.nanolett.5b02287

Volume: 1.5E+001 Issue: 8.0E+000 First Page #: 5597

Date Submitted:

Date Published:

Publication Location:

Article Title: Plasmonic Properties of Silicon Nanocrystals Doped with Boron and Phosphorus

Authors:

Keywords: Silicon, nanocrystals, doping, plasmonics

Abstract: Degenerately doped silicon nanocrystals are appealing plasmonic materials due to silicon's low cost and low toxicity. While surface plasmonic resonances of boron-doped and phosphorus-doped silicon nanocrystals were recently observed, there currently is poor understanding of the effect of surface conditions on their plasmonic behavior. Here, we demonstrate that phosphorus-doped silicon nanocrystals exhibit a plasmon resonance immediately after their synthesis but may lose their plasmonic response with oxidation. In contrast, boron-doped nanocrystals initially do not exhibit plasmonic response but become plasmonically active through postsynthesis oxidation or annealing. We interpret these results in terms of substitutional doping being the dominant doping mechanism for phosphorus-doped silicon nanocrystals, with oxidation-induced defects trapping free electrons. The behavior of boron-doped silicon nanocrystals is more consistent with a strong contribution of surface doping. Importantly, b

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Volume: 88

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Date Submitted: 9/1/16 12:00AM

Date Published: 8/1/16 5:00AM

Publication Location:

Article Title: Liquid Nebulization–Ion Mobility Spectrometry Based Quantification of Nanoparticle–Protein Conjugate Formation

Authors: Seongho Jeon, Derek R. Oberreit, Gary Van Schooneveld, Christopher J. Hogan

Keywords: Liquid Nebulizers, Ion Mobility Spectrometry,

Abstract: The most prominent change to a nanoparticle population upon conjugate formation is a shift in the nanoparticle size distribution function. However, commonly employed dynamic light scattering based approaches for size distribution characterization are ineffective for nonmonodisperse samples, and further they are relatively insensitive to size shifts of only several nanometers, which are common during conjugate formation. Conversely, gas phase ion mobility spectrometry (IMS) techniques can be used to reliably examine polydisperse samples, and are sensitive to ~1 nm size distribution function shifts; the challenge with IMS is to convert nanoparticle-protein conjugates to aerosol particles without bringing about nonspecific aggregation or conjugate formation. We specifically employ the LN-IMS system to examine bovine serum albumin binding to gold nanoparticles. Inferred maximum protein surface coverages (~0.025 nm²) from measurements are shown to be in agreement with reported QCM values

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Journal: Nano Letters

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Date Submitted: 9/1/16 12:00AM

Date Published: 2/1/16 6:00AM

Publication Location:

Article Title: Broadband Absorbing Exciton–Plasmon Metafluids with Narrow Transparency Windows

Authors: Jihua Yang, Nicolaas J. Kramer, Katelyn S. Schramke, Lance M. Wheeler, Lucas V. Besteiro, Christoph

Keywords: Colloidal boron-doped silicon nanocrystals, gold nanorods, exciton-plasmon metafluid, transparency window

Abstract: Optical metafluids consist of colloidal solutions of plasmonic and/or excitonic nanomaterials may play important roles as functional working fluids or as means for producing solid metamaterial coatings. We demonstrate water-based metafluids that act as broadband electromagnetic absorbers in a range of 200–3300 nm and feature tunable narrow transparency window in the visible-near-infrared region. To define this transparency window, we employ plasmonic gold nanorods. We utilize excitonic boron-doped silicon nanocrystals as opaque optical absorbers “optical wall” in the UV and blue-green range of the spectrum. Water itself acts as an opaque “wall” in the near-infrared to infrared. “simple” metafluid by computationally testing & validating the effective medium approach based on the Beer-Lambert law. According to simulations & experiments, particle aggregation and the associated decay of the window effect are one example of the failure of the simple metafluid due to strong interactions

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Date Submitted: 9/1/16 12:00AM

Date Published:

Publication Location:

Article Title: Nanomaterial size distribution analysis via liquid nebulization coupled with ion mobility spectrometry (LN-IMS)

Authors: Seongho Jeon, Derek R. Oberreit, Gary Van Schooneveld, Christopher J. Hogan

Keywords: Liquid Nebulization, Ion Mobility spectrometry with Differential mobility analyser

Abstract: We apply liquid nebulization (LN) in series with ion mobility spectrometry (IMS, using a differential mobility analyzer coupled to a condensation particle counter) to measure the size distribution functions (the number concentration per unit log diameter) of gold nanospheres in the 5–30 nm range, 70 nm × 1.7 nm gold nanorods, and albumin proteins originally in aqueous suspensions. Uniquely, the LN employed in this study uses both online dilution with ultra-high purity water and a ball-impactor to remove droplets larger than 500 nm in diameter. Through comparison to electron microscopy measurements, we find that the size distribution functions inferred via LN-IMS measurements correspond to the particle sizes coated by surfactants, i.e. as they persist in colloidal suspensions. Finally, we show that the gas phase particle concentrations inferred from IMS size distribution functions are functions of only of the liquid phase particle concentration, and are independent of particle size,

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Volume: 5

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Date Submitted: 9/1/16 12:00AM

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Publication Location:

Article Title: Self-assembly of plasmonic/excitonic silicon nanocrystals into photonic crystals

Authors: Jihua Yang, Nicolaas J. Kramer, Christopher J. Hogan, Uwe R. Kortshagen

Keywords: Boron doped Si Nanocrystals, Aerosolization

Abstract: In this work, photonic crystals of plasmonic/excitonic semiconductor nanocrystals (NCs) were assembled from non-thermal plasma-synthesized boron (B)-doped silicon (Si) NCs. The photonic crystals form an inverse opal structure with larger refractive index than the conventional crystals made from silica nanoparticles and are aimed at controlling light propagation via excitonic and plasmonic absorption of the B-doped Si NC as well as the photonic band gap of the photonic crystal. Furthermore, we demonstrate self-assembly of mesoscopic photonic crystal particles consisting of B-doped Si NCs with well-defined inverse opal structure via simple aerosol processing.

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Volume: 92

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Date Published: 2/1/16 6:00AM

Publication Location:

Article Title: Two dimensional size–mass distribution function inversion from differential mobility analyzer–aerosol particle mass analyzer (DMA–APM) measurements

Authors: Vivek K. Rawat, David T. Buckley, Shigeru Kimoto, Myong-Hwa Lee, Nobuhiko Fukushima, Christopher

Keywords: Data inversion routine Aerosol particle mass analyzer Differential mobility analyzer Size distribution function

Abstract: We developed and applied a data inversion routine to determine the number based size mass distribution function (the 2D distribution function) from tandem differential mobility analyzer–aerosol particle mass analyzer (DMA–APM) measurements. The 2D distribution function is expressed in units of particle number concentration per unit mobility diameter per unit particle mass. The inversion routine utilizes the Twomey–Markowski algorithm and is applied in this study to DMA–APM measurements of NaCl, CsI, and NH₄SO₄ particles in the 30–200 nm mobility diameter range. For the examined salt particles, visual representation of the 2D distribution function reveals that a given mobility diameter, particles have very narrow mass distributions, with the peak masses in good agreement with predictions. We determine the 2D distribution function for a mixture of ammonium sulfate and soot particles, demonstrating that these 2 particle populations are separable from one another via mobility-mass analysis.

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Journal: Nature Communications

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Publication Identifier: 10.1038/ncomms9379

Volume: 6

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Date Submitted: 9/2/16 12:00AM

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Publication Location:

Article Title: Circularly polarized light detection with hot electrons in chiral plasmonic metamaterials

Authors: Wei Li, Zachary J. Coppens, Lucas V. Besteiro, Wenyi Wang, Alexander O. Govorov, Jason Valentine

Keywords: circularly polarized light photodetector, chiral plasmonic metamaterials

Abstract: Circularly polarized light is utilized in various optical techniques and devices. But, using conventional optical systems to generate, analyse and detect circularly polarized light involves multiple optical elements, making it challenging to realize miniature and integrated devices. The development of an efficient and highly selective circularly polarized light photodetector remains challenging. Here we report on an ultracompact circularly polarized light detector that combines large engineered chirality, realized using chiral plasmonic metamaterials, with hot electron injection. We demonstrate the detector's ability to distinguish between left and right hand circularly polarized light without the use of additional optical elements. Implementation of this photodetector could lead to enhanced security in fibre and free-space communication, as well as emission, imaging and sensing applications for circularly polarized light using a highly integrated photonic platform.

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Volume: 7

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Date Submitted: 9/2/16 12:00AM

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Publication Location:

Article Title: A light-driven three-dimensional plasmonic nanosystem that translates molecular motion into reversible chiroptical function

Authors: Anton Kuzyk, Yangyang Yang, Xiaoyang Duan, Simon Stoll, Alexander O. Govorov, Hiroshi Sugiyama, I

Keywords: Plasmonic Nanosystems, DNA origami,

Abstract: Nature has developed striking light-powered proteins such as bacteriorhodopsin, which can convert light energy into conformational changes for biological functions. However, synthetic molecular machines typically operate at the nanometre scale or below. Translating controlled operation of individual molecular machines to a larger dimension, for example, to 10–100 nm, which features many practical applications, is highly important but remains challenging. Here we demonstrate a light-driven plasmonic nanosystem that can amplify the molecular motion of azobenzene through the host nanostructure and consequently translate it into reversible chiroptical function with large amplitude modulation. Light is exploited as both energy source and information probe. Our plasmonic nanosystem bears unique features of optical addressability, reversibility and modulability, which are crucial for developing all-optical molecular devices with desired functionalities.

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Journal: The Journal of Physical Chemistry C

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Volume: 120

Issue: 21

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Date Submitted: 9/2/16 12:00AM

Date Published: 6/1/16 5:00AM

Publication Location:

Article Title: Boosting Hot Electron-Driven Photocatalysis through Anisotropic Plasmonic Nanoparticles with Hot Spots in Au–TiO

Authors: Ana Sousa-Castillo, Miguel Comesaña-Hermo, Benito Rodríguez-González, Moisés Pérez-Lorenzo, Zhi

Keywords: Au-TiO₂ photoreactors Au nanostars

Abstract: The use of plasmonic metal nanoparticles as photosensitizers has undergone a strong development in the past few years given their ability to increase the activity of semiconductors into the visible and near-infrared regions. This work reports an experimental and theoretical study on the critical influence that shape anisotropy of gold nanoparticles exerts on the photocatalytic performance of Au/TiO₂ nanoarchitectures. The results show that for a given amount of metallic material, Au nanostars endow titania with an enhanced catalytic efficiency compared to that found in the presence of Au nanospheres or nanorods. This is due to the ability of nanostars to locally create extremely large electromagnetic field enhancements around their spikes, which ensures an increased population of hot electrons close to the interface between the metal and the semiconductor. These results pave the way for a more rational design of the plasmonic component for high-performance photocatalytic nanoreactors.

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Journal: The Journal of Physical Chemistry C

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Volume: 120

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Date Published: 6/1/16 10:00AM

Publication Location:

Article Title: Localization of Excess Temperature Using Plasmonic Hot Spots in Metal Nanostructures: Combining Nano-Optical Antennas with the Fano Effect

Authors: Larousse Khosravi Khorashad, Lucas V. Besteiro, Zhiming Wang, Jason Valentine, Alexander O. Govor

Keywords: Nanoparticle trimers, Localized excess temperature, photo thermal heating, Fano resonance.

Abstract: It is challenging to strongly localize temperature in small volumes because heat transfer is a diffusive process. Here we show how to overcome this limitation using electrodynamic hot spots and interference effects in the regime of CW excitation. We introduce a set of figures of merit for the localization of excess temperature and for the efficiency of the plasmonic photothermal effect. Our calculations show that the local temperature distribution in a trimer nanoparticle assembly is a complex function of the geometry and sizes. In the trimer assembly composed of a nanorod and two spherical nanoparticles, we observe a strong plasmonic Fano effect that leads to the concentration of optical energy in the small heater nanorod. Therefore, the power efficiency of generation of local excess temperature in the nanorod-based assembly greatly increases due to the strong plasmonic Fano effect

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Journal: Journal of the American Chemical Society

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Publication Identifier: 10.1021/jacs.6b04096

Volume: 138

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Date Submitted: 9/2/16 12:00AM

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Publication Location:

Article Title: DNA Scaffolds for the Dictated Assembly of Left-/Right-Handed Plasmonic Au NP Helices with Programmed Chiro-Optical Properties

Authors: Alessandro Cecconello, Jason S. Kahn, Chun-Hua Lu, Larousse Khosravi Khorashad, Alexander O. Govor

Keywords: DNA origami, Plasmonic Au nanoparticle helices, circular dichroism

Abstract: Within the broad interest of assembling chiral left- and right-handed helices of plasmonic nanoparticles (NPs), we introduce the DNA-guided organization of left- or right-handed plasmonic Au NPs on DNA scaffolds. The method involves the self-assembly of stacked 12 DNA quasi-rings interlinked by 30 staple-strands. By the functionalization of one group of staple units with programmed tether-nucleic acid strands and additional staple elements with long nucleic acid chains, acting as promoter strands, the promoter-guided assembly of barrels modified with 12 left- or right-handed tethers is achieved. The subsequent hybridization of Au NPs functionalized with single nucleic acid tethers yields left- or right-handed structures of plasmonic NPs. The plasmonic NP structures reveal CD spectra at the plasmon absorbance. Using geometrical considerations corresponding to the left and right-handed helices of the Au NPs, the experimental CD spectra of the plasmonic Au NPs are modeled.

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Journal: ACS Photonics

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Publication Identifier: 10.1021/acsp Photonics.5b00594

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Date Submitted: 9/2/16 12:00AM

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Publication Location:

Article Title: Electron Energy-Loss Spectroscopy of Multipolar Edge and Cavity Modes in Silver Nanosquares

Authors: Edson P. Bellido, Alejandro Manjavacas, Yue Zhang, Yang Cao, Peter Nordlander, Gianluigi A. Botton

Keywords: electron energy loss spectroscopy, surface plasmons, edge modes, cavity modes, local density of states, silver nanosquares

Abstract: In this work, we demonstrate the power of this technique for probing and imaging resonances of metallic nanostructures by analyzing the plasmonic response of silver nanosquares of sizes ranging from 230 nm up to 1 μ m. Because of the relatively large size of these structures, we find that, despite their simple geometry, these systems can support a large variety of multipolar modes, which can only be detected and imaged due to the high spatial and energy resolution achieved by pushing EELS to its limits. The experimental results are supported by theoretical calculations. In particular, we were able to map, with high level of detail, edge and high-order cavity modes. Also, by calculating the scattering cross-section of these nanostructures, we confirm that most of the observed modes are dark and thus remain hidden in optical measurements, thus demonstrating the power of EELS as a unique tool for probing and imaging a large range and variety of plasmonic resonances of nanostructures

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Date Submitted: 9/2/16 12:00AM

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Publication Location:

Article Title: Chiral and Achiral Nanodumbbell Dimers: The Effect of Geometry on Plasmonic Properties

Authors: Kyle W. Smith, Hangqi Zhao, Hui Zhang, Ana Sánchez-Iglesias, Marek Grzelczak, Yumin Wang, Wei-St

Keywords: chiroptical activity, single-particle spectroscopy, localized surface plasmons, self-assembly, gold nanoparticles

Abstract: Metal nanoparticles with a dumbbell-like geometry have plasmonic properties similar to those of their nanorod counterparts, but the unique steric constraints induced by their enlarged tips result in distinct geometries when self-assembled. Here, we investigate gold dumbbells that are assembled into dimers within polymeric micelles. A single-particle approach with correlated scanning electron microscopy and dark-field scattering spectroscopy reveals the effects of dimer geometry variation on the scattering properties. Experiments and detailed simulations confirm the influence of various symmetry elements on the overall peak resonance energy, spectral line shape, and circular differential scattering response. This work expands understanding of the influence self-assembled geometries have on plasmonic properties, particularly with regard to racemic samples which may have significant optical activity that may be overlooked when using exclusively ensemble characterization techniques

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Journal: The Journal of Physical Chemistry C

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Volume: Issue:

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Date Submitted: 9/2/16 12:00AM

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Publication Location:

Article Title: Laser-Induced Spectral Hole-Burning through a Broadband Distribution of Au Nanorods

Authors: Christopher J. DeSantis, Da Huang, Hui Zhang, Nathaniel J. Hogan, Hangqi Zhao, Yifei Zhang, Alejandra

Keywords: Au Nanorods, fs pulsed laser, transmission window

Abstract: Nanorods are amenable to laser-induced reshaping, a process that can dramatically modify their shape and therefore their plasmonic properties. Here we show that when a broadband spectral distribution of nanorods is irradiated with a femtosecond-pulsed laser, an optical transmission window is formed in the extinction spectrum. Surprisingly, the transmission window that is created does not occur at the laser wavelength but rather is consistently shifted to longer wavelengths, and the optical extinction on the short-wavelength side of the transmission window is increased by the hole-burning process. We develop a straightforward theoretical model that explains how the spectral position, depth, and width of the laser-induced transmission window are controlled by laser irradiation conditions. This work serves as an initial example of laser-based processing of specially designed nanocomposite media to create new materials with "written-in" optical transmission characteristics.

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Journal: ACS Photonics

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Publication Location:

Article Title: Asymmetric Aluminum Antennas for Self-Calibrating Surface-Enhanced Infrared Absorption Spectroscopy

Authors: Benjamin Cerjan, Xiao Yang, Peter Nordlander, Naomi J. Halas

Keywords: SEIRA, FTIR, aluminum, internal calibration, nanoantenna

Abstract: There has been a tremendous recent interest in noble metal-based antennas as substrates for surface-enhanced infrared absorption spectroscopy, more abundant and manufacturable metals may offer similar or additional opportunities for this mid-infrared sensing modality. We examine the feasibility of aluminum antennas for SEIRA, by designing and fabricating asymmetric aluminum cross antennas with nanometer-scale gaps. The asymmetric cross design enables the simultaneous detection of multiple infrared vibrational resonances over a broad region of the midinfrared spectrum. The presence of the Al₂O₃ surface oxide layer not only passivates the metal antenna structures but also enables a very straightforward covalent binding chemistry for analyte molecules to the antenna through multiple approaches, in this case by the use of carboxylic acid functional groups. The Al - O stretching mode of the oxide can be used as a self-calibration standard to quantify the number of analyte molecules.

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Publication Location:

Article Title: Nanooptics of Plasmonic Nanomatryoshkas: Shrinking the Size of a Core–Shell Junction to Subnanometer

Authors: Li Lin, Mario Zapata, Min Xiong, Zhonghui Liu, Shanshan Wang, Hong Xu, Andrei G. Borisov, Hongcher

Keywords: Plasmon, nanoshells, quantum plasmonics, tunneling plasmon

Abstract: Quantum effects in plasmonic systems play an important role in defining the optical response of structures with subnanometer gaps. Electron tunneling across the gaps can occur, altering both the far-field optical response and the near-field confinement and enhancement. In this study, we experimentally and theoretically investigate plasmon coupling in gold “nanomatryoshka” (NM) nanoparticles with different core-shell separations. Plasmon coupling effects between the core and the shell become significant when their separation decreases to 15 nm. When their separation decreases to below 1 nm, the near- and far-field properties can no longer be described by classical approaches but require the inclusion of quantum mechanical effects such as electron transport through the self-assembled monolayer of molecular junction. Our quantum modeling provides an estimate for the AC conductances of molecules in the junction.

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Date Submitted: 9/2/16 12:00AM

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Publication Location:

Article Title: Pronounced Linewidth Narrowing of an Aluminum Nanoparticle Plasmon Resonance by Interaction with an Aluminum Metallic Film

Authors: Ali Sobhani, Alejandro Manjavacas, Yang Cao, Michael J. McClain, F. Javier García de Abajo, Peter No

Keywords: Aluminum, plasmons, nanoparticle, film, radiative losses

Abstract: Aluminum nanocrystals and fabricated nanostructures are emerging as highly promising building blocks for plasmonics in the visible region of the spectrum. Even at the individual nanocrystal level, however, the localized plasmons supported by Al nanostructures possess a surprisingly broad spectral response. We have observed that when an Al nanocrystal is coupled to an underlying Al film, its dipolar plasmon resonance linewidth narrows remarkably and shows an enhanced scattering efficiency. This is far more dramatic in the aluminum nanoparticle-film system, reducing the dipolar plasmon linewidth by more than half. A substrate-mediated hybridization of the dipolar and quadrupolar plasmons of the nanoparticle reduces the radiative losses of the dipolar plasmon. While this is a general effect that applies to all metallic nanoparticle-film systems, this finding specifically provides a new mechanism for narrowing plasmon resonances in aluminum-based systems

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Volume: 112 Issue: 40

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Date Submitted: 9/2/16 12:00AM

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Publication Location:

Article Title: Single quantum dot controls a plasmonic cavity's scattering and anisotropy

Authors: Thomas Hartsfield, Wei-Shun Chang, Seung-Cheol Yang, Tzuhsuan Ma, Jinwei Shi, Liuyang Sun, Genr

Keywords: optical spectroscopy, hybrid nanostructures, quantum systems, plasmonic cavities, Fano resonance

Abstract: Plasmonic cavities represent a promising platform for controlling light-matter interaction due to their exceptionally small mode volume and high density of photonic states. Using plasmonic cavities for enhancing light's coupling to individual two-level systems, such as single semiconductor quantum dots (QD), is particularly desirable for exploring cavity quantum electrodynamics (QED) effects and using them in quantum information applications. Here, we study the simplest plasmonic cavity in the form of a spherical metallic nanoparticle (MNP). By controllably positioning a semiconductor QD in the close proximity of the MNP cavity via atomic force microscope (AFM) manipulation, the scattering spectrum of the MNP is dramatically modified due to Fano interference between the classical plasmonic resonance of the MNP and the quantized exciton resonance in the QD. Moreover, our experiment demonstrates that a single two-level system can render a spherical MNP strongly anisotropic

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Volume: 2 Issue: 11

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Date Submitted: 9/2/16 12:00AM

Date Published: 11/1/15 5:00AM

Publication Location:

Article Title: Circular Differential Scattering of Single Chiral Self-Assembled Gold Nanorod Dimers

Authors: Lin-Yung Wang, Kyle W. Smith, Sergio Dominguez-Medina, Nicole Moody, Jana M. Olson, Huanan Zha

Keywords: chirality, nanoparticle, surface plasmon, self-assembly, single-particle spectroscopy

Abstract: Circular dichroism spectroscopy is essential for structural characterization of proteins and chiral nanomaterials. Chiral structures from plasmonic materials have extraordinary strong circular dichroism effects compared to their molecular counterparts. Here we investigated the circular differential scattering of a simple chiral plasmonic system, a twisted side-by-side Au nanorod dimer, using single-particle circular dichroism spectroscopy complemented with electromagnetic simulations. Our results demonstrate that, if only scattering is considered as measured by dark-field spectroscopy, a homodimer of Au nanorods with similar sizes produces a CD scattering line shape that is different from the bisignate response of the corresponding conventional CD spectrum, which measures extinction, that is, the sum of scattering and absorption. Symmetry breaking in a heterodimer with Au nanorods with different sizes yields a bisignate circular differential scattering line shape.

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Date Submitted: 9/2/16 12:00AM

Date Published: 12/1/15 6:00AM

Publication Location:

Article Title: Single-Crystalline Copper Nano-Octahedra

Authors: Shu-Chen Lu, Ming-Cheng Hsiao, Mustafa Yorulmaz, Lin-Yung Wang, Po-Yuan Yang, Stephan Link, W

Keywords: Al₂O₃ passivated Cu Nano octahedra

Abstract: Single-crystalline Cu nano-octahedra with welldefined edge lengths were synthesized successfully via a hotinjection method using TOP as capping ligand. The nanooctahedra tend to self-assemble into HCP arrays and their assembled structure is here confirmed via SEM and TEM. Furthermore, the optical properties of as-prepared Cu nanooctahedra were investigated both experimentally and theoretically

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Journal: Proceedings of the National Academy of Sciences

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Volume: 113

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Date Submitted: 9/2/16 12:00AM

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Publication Location:

Article Title: Imaging through plasmonic nanoparticles

Authors: Mehbuba Tanzid, Ali Sobhani, Christopher J. DeSantis, Yao Cui, Nathaniel J. Hogan, Adam Samaniego

Keywords: light scattering, imaging, nanoparticles, plasmonics, metamaterials

Abstract: The optical properties of metallic nanoparticles with plasmon resonances have been studied extensively, typically by measuring the transmission of light, as a function of wavelength, through a nanoparticle suspension. One question that has not yet been addressed, however, is how an image is transmitted through such a suspension of absorber-scatterers, in other words, how the various spatial frequencies are attenuated as they pass through the nanoparticle host medium. Here, we examine how the optical properties of a suspension of plasmonic nanoparticles affect the transmitted image. We show that perceived image quality, as well as spatial resolution, are both dependent on the scattering and absorption cross-sections of the constituent nanoparticles. Surprisingly, we observe a nonlinear dependence of image quality on optical density by varying optical path length and nanoparticle concentration.

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Volume: 9

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Date Submitted: 9/2/16 12:00AM

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Publication Location:

Article Title: Fano Resonant Aluminum Nanoclusters for Plasmonic Colorimetric Sensing

Authors: Nicholas S. King, Lifei Liu, Xiao Yang, Benjamin Cerjan, Henry O. Everitt, Peter Nordlander, and Naomi

Keywords: plasmon . aluminum . ultraviolet . Fano resonance . chromaticity . figure of merit

Abstract: Aluminum is an abundant and high-quality material for plasmonics with potential for large-area, low-cost photonic technologies. Here we examine aluminum nanoclusters with plasmonic Fano resonances that can be tuned from the near-UV into the visible region of the spectrum. These nanoclusters can be designed with specific chromaticities in the bluegreen region of the spectrum and exhibit a remarkable spectral sensitivity to changes in the local dielectric environment. We show that such structures can be used quite generally for colorimetric localized surface plasmon resonance (LSPR) sensing, where the presence of analytes is detected by directly observable color changes rather than through photodetectors and spectral analyzers. To quantify our results and provide a metric for optimization of such structures for colorimetric LSPR sensing, we introduce a figure of merit based on the color perception ability of the human eye.

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Volume: 17

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Date Submitted: 10/23/17 12:00AM

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Publication Location:

Article Title: Ultrafast Silicon Photonics with Visible to Mid-Infrared Pumping of Silicon Nanocrystals

Authors: Benjamin T. Diroll, Katelyn S. Schramke, Peijun Guo, Uwe R. Kortshagen, Richard D. Schaller

Keywords: Silicon photonics, optical switching, infrared, plasmonics, doping

Abstract: Dynamic optical control of infrared (IR) transparency and refractive index is achieved using boron-doped silicon nanocrystals excited with mid-IR optical pulses. Unlike previous silicon-based optical switches, large changes in transmittance are achieved without a fabricated structure by exploiting strong light coupling of the localized surface plasmon resonance (LSPR) produced from free holes of p-type silicon nanocrystals. The choice of optical excitation wavelength allows for selectivity between hole heating and carrier generation through intraband or interband photoexcitation, respectively. Mid-IR optical pumping heats the free holes of p-Si nanocrystals to effective temperatures greater than 3500 K. Increases of the hole effective mass at high effective hole temperatures lead to a subpicosecond change of the dielectric function, resulting in a redshift of the LSPR, modulating mid-IR transmission by as much as 27%, and increasing the index of refraction by more than 0.1 in the mid-IR.

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Date Submitted: 10/23/17 12:00AM

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Publication Location:

Article Title: Doped Silicon Nanocrystal Plasmonics

Authors: Hui Zhang, Runmin Zhang, Katelyn S. Schramke, Nicholas M. Bedford, Katharine Hunter, Uwe R. Korts

Keywords: silicon nanocrystals, quantum dots, plasmonics, plasmon hybridization

Abstract: Doped semiconductor nanocrystals represent an exciting new type of plasmonic material with optical resonances in the infrared. Unlike noble metal nanoparticles, the plasmon resonance can be tuned by altering the doping density. Recently, it has been shown that silicon nanocrystals can be doped using phosphorus and boron resulting in highly tunable infrared plasmon resonances. Due to the band structure of silicon, doping with phosphorus contributes light (transverse) and heavy (longitudinal) electrons, while boron contributes light and heavy holes and one would expect two distinct plasmon branches. Here we develop a classical hybridization theory and a full quantum mechanical TDLDA approach for two-component carrier plasmas and show that the interaction between the two plasmon branches results in strongly hybridized plasmon modes. The antibonding mode where the two components move in phase is bright and depends sensitively on the doping densities.

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Date Submitted: 12/20/18 12:00AM

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Publication Location:

Article Title: Vibrational coupling in plasmonic molecules

Authors: Chongyue Yi, Pratiksha D. Dongare, Man-Nung Su, Wenxiao Wang, Debadi Chakraborty, Fangfang We

Keywords: plasmonics; Coherent phonon; ultrafast spectroscopy; optomechanics

Abstract: Plasmon hybridization theory, inspired by molecular orbital theory, has been extremely successful in describing the near-field coupling in clusters of plasmonic nanoparticles, also known as plasmonic molecules. However, the vibrational modes of plasmonic molecules have been virtually unexplored. By designing precisely configured plasmonic molecules of varying complexity and probing them at the individual plasmonic molecule level, intramolecular coupling of acoustic modes, mediated by the underlying substrate, is observed. The strength of this coupling can be manipulated through the configuration of the plasmonic molecules. Surprisingly, classical continuum elastic theory fails to account for the experimental trends, which are well described by a simple coupled oscillator picture that assumes the vibrational coupling is mediated by coherent phonons with low energies. These findings provide a route to the systematic optical control of the gigahertz response of metallic nanostructures.

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Volume: 9

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Date Submitted: 10/23/17 12:00AM

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Publication Location:

Article Title: Self-assembly of nanoparticles into biomimetic capsid-like nanoshells

Authors: Ming Yang, Henry Chan, Gongpu Zhao, Joong Hwan Bahng, Peijun Zhang, Petr Král, Nicholas A. Kotov

Keywords: Biocatalysis; Nanoparticles

Abstract: Nanoscale compartments are one of the foundational elements of living systems. Capsids, carboxysomes, exosomes, vacuoles and other nanoshells easily self-assemble from biomolecules such as lipids or proteins, but not from inorganic nanomaterials because of difficulties with the replication of spherical tiling. Here we show that stabilizer-free polydispersed inorganic nanoparticles (NPs) can spontaneously organize into porous nanoshells. The association of water-soluble CdS NPs into self-limited spherical capsules is the result of scale-modified electrostatic, dispersion and other colloidal forces. They cannot be accurately described by the Derjaguin–Landau–Verwey–Overbeek theory, whereas molecular-dynamics simulations with combined atomistic and coarse-grained description of NPs reveal the emergence of nanoshells and some of their stabilization mechanisms. Morphology of the simulated assemblies formed under different conditions matched nearly perfectly the transmission electron microsc

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Volume: 16

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Date Submitted: 10/23/17 12:00AM

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Publication Location:

Article Title: Absorption Spectroscopy of an Individual Fano Cluster

Authors: Mustafa Yorulmaz, Anneli Hoggard, Hangqi Zhao, Fangfang Wen, Wei-Shun Chang, Naomi J. Halas, Pe

Keywords: Surface plasmons, Fano resonance, near-field coupling, single-particle spectroscopy, photothermal imaging

Abstract: Plasmonic clusters can exhibit Fano resonances with unique and tunable asymmetric line shapes. These structures are capable of generating remarkably large local electromagnetic field enhancements and should give rise to high hot carrier yields relative to other plasmonic nanostructures. While the scattering properties of individual plasmonic Fano resonances have been characterized extensively, their absorption properties, critical for hot carrier generation, have not yet been measured. Here, we utilize single-particle absorption spectroscopy based on photothermal imaging to distinguish between the radiative and nonradiative properties of an individual Fano cluster. In observing the absorption spectrum of individual Fano clusters, we directly verify the theoretical prediction that while Fano interference may be prominent in scattering, it is completely absent in absorption.

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Date Submitted: 10/23/17 12:00AM

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Publication Location:

Article Title: Plasmonic colour generation

Authors: Anders Kristensen, Joel K. W. Yang, Sergey I. Bozhevolnyi, Stephan Link, Peter Nordlander, Naomi J. Halas

Keywords: Metamaterials; Nanophotonics and plasmonics; Optical materials and structures; Sub-wavelength optics

Abstract: Plasmonic colors are structural colors that emerge from resonant interactions between light and metallic nanostructures. The engineering of plasmonic colors is a promising, rapidly emerging research field that could have a large technological impact. We highlight basic properties of plasmonic colors and recent nanofabrication developments, comparing technology-performance indicators for traditional and nanophotonic color technologies. The structures of interest include diffraction gratings, nanoaperture arrays, thin films, and multilayers and structures that support Mie resonances and whispering-gallery modes. We discuss plasmonic color nanotechnology based on localized surface plasmon resonances, such as gap plasmons and hybridized disk-hole plasmons, which allow for color printing with sub-diffraction resolution. We also address a range of fabrication approaches that enable large-area printing and nanoscale lithography compatible with complementary metal-oxide semiconductor technology

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Date Submitted: 10/23/17 12:00AM

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Publication Location:

Article Title: Optomechanics of Single Aluminum Nanodisks

Authors: Man-Nung Su, Pratiksha D. Dongare, Debadi Chakraborty, Yue Zhang, Chongyue Yi, Fangfang Wen, W. G. J. van der Wiel

Keywords: : Acoustic vibrations, aluminum nanostructures, nanomechanics, ultrafast spectroscopy, single-particle spectroscopy

Abstract: Aluminum nanostructures support tunable surface plasmon resonances and have become an alternative to gold nanoparticles. In addition to understanding the size and shape tunability of the plasmon resonance, the fundamental relaxation processes in aluminum nanostructures after photoexcitation must be understood to take full advantage of applications such as photocatalysis and photodetection. We investigate the relaxation following ultrafast pulsed excitation and the launching of acoustic vibrations in individual aluminum nanodisks, using single-particle transient extinction spectroscopy. We find that the transient extinction signal can be assigned to a thermal relaxation of the photoexcited electrons and phonons. The ultrafast heating-induced launching of in-plane acoustic vibrations reveals moderate binding to the glass substrate and is affected by the native aluminum oxide layer. Finally, we compare the behavior of aluminum nanodisks to that of similarly prepared and sized gold nanodisks

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Volume: 32 **Issue:** **First Page #:** 40
Date Submitted: 10/23/17 12:00AM **Date Published:** 9/1/17 5:00AM
Publication Location:

Article Title: Optical characterization of chiral plasmonic nanostructures

Authors: Kyle W. Smith, Stephan Link, Wei-Shun Chang

Keywords: Chirality Localized surface plasmons Single particle spectroscopy Nonlinear spectroscopy Near-field optical microscopy

Abstract: Chiral plasmonic nanomaterials can have circular dichroism and optical rotatory dispersion effects orders of magnitude larger than those observed in ordinary chiral molecules. Understanding this fascinating class of materials has proved challenging and has motivated several research groups to develop entirely new experimental techniques for characterizing chirality driven optical properties. In this review, we first describe the classical method of circular dichroism which measures linear, far-field responses from an ensemble population. We then go on to describe several of the more recently developed methods to probe chiral nanostructures as they expand into the domains of non-linear, near-field, and single particle measurements including spatially and spectrally resolved techniques.

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Publication Identifier Type: DOI **Publication Identifier:** 10.1021/acs.jpcc.7b08428
Volume: **Issue:** **First Page #:**
Date Submitted: 10/23/17 12:00AM **Date Published:** 10/1/17 5:00AM
Publication Location:

Article Title: Environmental Symmetry Breaking Promotes Plasmon Mode Splitting in Gold Nanotriangles

Authors: Kyle W. Smith, Jian Yang, Taylor Hernandez, Dayne F. Swearer, Leonardo Scarabelli, Hui Zhang, Hang

Keywords: single particle spectroscopy; Au Triangle nanoparticles; FEM

Abstract: We report a single particle investigation of the polarized scattering spectra of individual Au nanotriangles (NTs) of the truncated bifrustum type. We unexpectedly observed a wide diversity in the scattering spectra from a population of NTs with low shape polydispersity. Correlation of the optical measurements with electron microscopy revealed that the different optical responses were not due to distinct NT shapes. Rather, finite element simulations revealed that distinct polarized spectra originated from minute changes in the inclination of the NTs on the substrate. NT inclination resulted in asymmetric image charge formation in the substrate, thus, breaking the degeneracy of the modes supported by the NTs. The degeneracy of the NT modes was extremely sensitive to such symmetry breaking, with inclination angles as small as 2°, producing clearly resolved, nondegenerate, and orthogonally polarized plasmon modes.

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Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI **Publication Identifier:** 10.1021/jacs.7b07838
Volume: **Issue:** **First Page #:**
Date Submitted: 10/23/17 12:00AM **Date Published:** 10/1/17 5:00AM
Publication Location:
Article Title: Template-Free Hierarchical Self-Assembly of Iron Diselenide Nanoparticles into Mesoscale Hedgehogs
Authors: Dawei Deng, Changlong Hao, Soumyo Sen, Chuanlai Xu, Petr Kral, Nicholas A. Kotov
Keywords: biomimetic nanoparticles, iron diselenide, nanosheets, nanoscrolls, multistage self-assembly, biomimetic superstructures, pyrite, nanoscale asymmetry
Abstract: The ability of semiconductor nanoparticles (NPs) to self-assemble has been known for several decades. However, the limits of the geometrical and functional complexity for the self-assembled nanostructures made from simple convex NPs are still continuing to amaze the researchers. We report here the self-assembly of primary ~2-4 nm FeSe₂ nanoparticles (NPs) with puck-like shapes either into (a) monocrystalline nanosheets ~5.5 nm thick, and ~1000 nm in lateral dimensions or (b) mesoscale hedgehogs ~550 nm in diameter with the spikes of ~250 nm in length, and ~10-15 nm, for high and low concentration of dodecanethiol (DT) in the reaction media. The nanosheets represent the constitutive part of hedgehogs. They are rolled into scrolls and assembled around a single core with distinct radial orientation forming nanoscale 'needles' approximately doubling its fractal dimension of these objects. The core is assembled from primary NPs and nanoribbons. Size distribution of the mesoscale hedgehogs i
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nano Letters
Publication Identifier Type: DOI **Publication Identifier:** 10.1021/acs.nanolett.7b02350
Volume: 17 **Issue:** 10 **First Page #:** 6034
Date Submitted: 10/23/17 12:00AM **Date Published:** 9/1/17 5:00AM
Publication Location:
Article Title: Two-Dimensional Active Tuning of an Aluminum Plasmonic Array for Full-Spectrum Response
Authors: Ming Lun Tseng, Jian Yang, Michael Semmlinger, Chao Zhang, Peter Nordlander, Naomi J. Halas
Keywords: Stretchable plasmonics, full-color tuning, aluminum plasmonics, active image switching, full color display, dynamic color display
Abstract: Color pixels composed of plasmonic nanostructures provide a highly promising approach for new display technologies, capable of vivid, robust coloration and incorporating the use of low-cost plasmonic materials, such as aluminum. Here we report a plasmonic device that can be tuned continuously across the entire visible spectrum, based on integrating a square array of aluminum nanostructures into an elastomeric substrate. By stretching the substrate in either of its two dimensions, the period and therefore the scattering color can be modified to the blue or the red of the at-rest structure, spanning the entire visible spectrum. The unique two-dimensional design of this structure enables active mechanical color tuning, under gentle elastic modulation with no more than 35% strain. We also demonstrate active image switching with this structure. This design strategy has the potential to open the door for nextgeneration flexible photonic devices for a wide variety of visible-light application
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Date Submitted: 10/23/17 12:00AM

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Publication Location:

Article Title: Aluminum Nanocrystals: A Sustainable Substrate for Quantitative SERS-Based DNA Detection

Authors: Shu Tian, Oara Neumann, Michael J. McClain, Xiao Yang, Linan Zhou, Chao Zhang, Peter Nordlander,

Keywords: Aluminum, nanocrystals, SERS, DNA, aggregates

Abstract: Since its discovery in the 1970s, surface-enhanced Raman scattering (SERS) has been primarily associated with substrates composed of nanostructured noble metals. Here we investigate chemically synthesized nanocrystal aggregates of aluminum, an inexpensive, highly abundant, and sustainable metal, as SERS substrates. Al nanocrystal aggregates are capable of substantial near-infrared SERS enhancements, similar to Au nanoparticles. The intrinsic nanoscale surface oxide of Al nanocrystals supports molecule/substrate interactions that differ dramatically from noble metal substrates. The preferential affinity of the single-stranded DNA (ssDNA) phosphate backbone for the Al oxide surface preserves both the spectral features and nucleic acid cross sections relative to conventional Raman spectroscopy, enabling quantitative ssDNA detection and analysis.

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Date Submitted: 10/23/17 12:00AM

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Publication Location:

Article Title: Abiotic tooth enamel

Authors: Bongjun Yeom, Trisha Sain, Naida Lacevic, Daria Bukharina, Sang-Ho Cha, Anthony M. Waas, Ellen M.

Keywords: Mechanical properties Synthesis and processing Mechanical engineering Bioinspired materials

Abstract: Tooth enamel comprises parallel microscale and nanoscale ceramic columns or prisms interlaced with a soft protein matrix^{1, 2, 3}. This structural motif is unusually consistent across all species from all geological eras^{4, 5, 6}. Such invariability—especially when juxtaposed with the diversity of other tissues—suggests the existence of a functional basis. Here we performed ex vivo replication of enamel-inspired columnar nanocomposites by sequential growth of zinc oxide nanowire carpets followed by layer-by-layer deposition of a polymeric matrix around these. We show that the mechanical properties of these nanocomposites, including hardness, are comparable to those of enamel despite the nanocomposites having a smaller hard-phase content. Our abiotic enamels have viscoelastic figures of merit (VFOM) and weight-adjusted VFOM that are similar to, or higher than, those of natural tooth enamels—we achieve values that exceed the traditional materials limits of 0.6 and 0.8, respectively.

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Date Submitted: 10/23/17 12:00AM

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Publication Location:

Article Title: Nanogapped Au Antennas for Ultrasensitive Surface-Enhanced Infrared Absorption Spectroscopy

Authors: Liangliang Dong, Xiao Yang, Chao Zhang, Benjamin Cerjan, Linan Zhou, Ming Lun Tseng, Yu Zhang, A

Keywords: bowtie antenna; FTIR; mixed self-assembled monolayers; nanogap; SEIRA

Abstract: Surface-enhanced infrared absorption (SEIRA) spectroscopy has outstanding potential in chemical detection as a complement to surface-enhanced Raman spectroscopy (SERS), yet it has historically lagged well behind SERS in detection sensitivity. Here we report a new ultrasensitive infrared antenna designed to bring SEIRA spectroscopy into the few-molecule detection range. Our antenna consists of a bowtie-shaped Au structure with a sub-3 nm gap, positioned to create a cavity above a reflective substrate. This three-dimensional geometry tightly confines incident mid-infrared radiation into its ultrasmall junction, yielding a hot spot with a theoretical SEIRA enhancement factor of more than 107, which can be designed to span the range of frequencies useful for SEIRA. We quantitatively evaluated the IR detection limit of this antenna design using mixed monolayers of 4-nitrothiophenol (4-NTP) and 4-methoxythiophenol (4-MTP). The optimized antenna structure allows the detection of as few as 25

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Volume: 3

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Date Submitted: 10/23/17 12:00AM

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Publication Location:

Article Title: Absorption-Induced Image Resolution Enhancement in Scattering Media

Authors: Mehbuba Tanzid, Nathaniel J. Hogan, Ali Sobhani, Hossein Robatjazi, Adithya K. Pediredla, Adam Sam

Keywords: absorption; diffusive transport; imaging; light scattering; resolution

Abstract: Highly scattering media pose significant challenges for many optical imaging applications due to the loss of information inherent to the scattering process. Absorption can also result in significant degradation of image quality. However, absorption can actually improve the resolution of images transmitted through scattering media in certain cases. Here we study how the presence of absorption can enhance the quality of an image transmitted through a scattering medium, by investigating the dependence of this enhancement on the medium's scattering properties. We find that absorption-induced image resolution enhancement is substantially larger for media consisting of isotropic scatterers (e.g., dielectric nanoparticles) than for strongly forward-scattering media (e.g., biological tissue). This work leads to a broader understanding, and ultimately control, of the optical properties of strongly absorbing, scattering media.

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Publication Identifier Type: DOI **Publication Identifier:** 10.1103/PhysRevE.96.032911
Volume: 96 **Issue:** 3 **First Page #:**
Date Submitted: 10/23/17 12:00AM **Date Published:** 9/1/17 5:00AM
Publication Location:

Article Title: Collision rate coefficient for charged dust grains in the presence of linear shear

Authors: Huan Yang, Christopher J. Hogan

Keywords: laminar shear; electrostatic potential interactions; particle-particle collision rate coefficient

Abstract: Like and oppositely charged particles or dust grains in linear shear flows are often driven to collide with one another by fluid and/or electrostatic forces, which can strongly influence particle-size distribution evolution. In gaseous media, collisions in shear are further complicated because particle inertia can influence differential motion. Expressions for the collision rate coefficient have not been developed previously which simultaneously account for the influences of linear shear, particle inertia, and electrostatic interactions. Here, we determine the collision rate coefficient accounting for the aforementioned effects by determining the collision area, i.e., the area of the plane perpendicular to the shear flow defining the relative initial locations of particles which will collide with one another. Integration of the particle flux over this area yields the collision rate. Collision rate calculations are parametrized as an enhancement factor, i.e., the ratio of the collision

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Volume: 18 **Issue:** 2 **First Page #:** 1234
Date Submitted: 12/20/18 12:00AM **Date Published:** 1/1/18 6:00PM
Publication Location:

Article Title: Aluminum Nanorods

Authors: Benjamin D. Clark, Christian R. Jacobson, Minhan Lou, Jian Yang, Linan Zhou, Sam Gottheim, Christop

Keywords: Anisotropic, nanocrystals, synthesis, dark-field spectroscopy, plasmonics

Abstract: Al nanocrystals can be synthesized by high-temperature decomposition of triisobutyl aluminum, creating a mixture of nanoparticle geometries with a significant fraction (~15%) being single-crystalline Al nanorods. The Al nanorods are elongated along their [110] direction, and generally exhibit hexagonal cross sections consisting of two adjacent {111} facets separated by {100} facets on opposite sides. Dark-field scattering spectroscopy of individual Al nanorods reveals that rods of varying aspect ratios all possess transverse quadrupolar and octupolar modes in the visible (2-3 eV) and ultraviolet (3-5 eV) regimes. Theoretical modeling indicates that the longitudinal resonances of these nanorods span the near- and mid-infrared regions of the spectrum. This work introduces a new class of anisotropic metal nanocrystals composed of single-crystalline Al, opening the door to highly modifiable plasmonic nanorods from Earth-abundant metals.

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Volume: 20

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Date Submitted: 12/20/18 12:00AM

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Publication Location:

Article Title: Absorption-enhanced imaging through scattering media using carbon black nano-particles: from visible to near infrared wavelengths

Authors: Mehbuba Tanzid, Nathaniel J Hogan, Hossein Robatjazi, Ashok Veeraraghavan, Naomi J Halas

Keywords: imaging, light scattering, absorber particles, absorber, nanoparticles, carbon black

Abstract: Imaging through scattering media can be improved with the addition of absorbers. The image resolution enhancement is substantially greater when imaging through isotropic scatterers than when imaging through an ensemble of strongly forward scattering particles. Since the angular scattering distribution is determined by the size of the scatterers with respect to the wavelength of incident light, particles that are forward scatterers at visible wavelengths can be isotropic scatterers at in IR wavelengths. Here, we show that substantial image resolution enhancement can be achieved in the NIR wavelength regime for particles that are forward scattering at visible wavelengths using carbon black nanoparticles as a broadband absorber. This observation provides a new strategy for image enhancement through scattering media by selecting the appropriate wavelength range for imaging, in this case the near-IR, the addition of absorbers more effectively enhances the image resolution.

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Journal: ACS Photonics

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Publication Identifier: 10.1021/acsp Photonics.7b01514

Volume: 5

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Date Submitted: 12/20/18 12:00AM

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Publication Location:

Article Title: Work Function-Driven Hot Electron Extraction in a Bimetallic Plasmonic MIM Device

Authors: Vårin R. A. Holm, Bob Y. Zheng, Phil M. Denby, Bodil Holst, Naomi J. Halas, Martin M. Greve

Keywords: LSPR EBL, Zero Bias, photocurrent, nanorods

Abstract: The Localized Surface Plasmon Resonance (LSPR) can cause hot electrons to be emitted from metal nanostructures. A key issue is how these hot electrons can be efficiently extracted and used for example in energy harvesting or sensing applications. One way is to create a plasmonic metal/insulator/metal device (MIM). In a plasmonic MIM device hot electrons (or holes) are injected from a nanostructured surface electrode across the insulator into the back electrode, and a current flows. Here we present a new, bimetallic plasmonic MIM device where the different work functions of the metal electrodes result in a built-in electrical field which facilitates hot electron extraction. This eliminates the need for an externally applied bias. The nanostructured front electrode, with 52 nm wide and 10 μ m long gold nanorods, is separated from the back electrode of aluminum by an insulator layer of Al₂O₃ with thicknesses varying between 3 and 18 nm. A maximum device responsivity of about 2.2 μ A/W is measured.

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Date Submitted: 12/20/18 12:00AM

Date Published: 8/1/18 5:00AM

Publication Location:

Article Title: Combining Plasmonic Hot Carrier Generation with Free Carrier Absorption for High-Performance Near-Infrared Silicon-Based Photodetection

Authors: Mehbuba Tanzid, Arash Ahmadiwand, Runmin Zhang, Ben Cerjan, Ali Sobhani, Sadegh Yazdi, Peter Nc

Keywords: plasmonics, hot carriers, free carrier absorption, near-infrared photodetector, silicon

Abstract: Plasmonic hot-carrier-based photodetectors detect light at frequencies below the semiconductor bandgap with room temperature operation and can exhibit spectrally narrowband behavior, potentially eliminating the need for bulky filtering or dispersive optics. This photodetection mechanism has, however, been plagued with low responsivities. Here we combine hot-carrier-based photodetection with free-carrier absorption (FCA) in highly doped p-type Si to create a narrowband, near-infrared, photodetector architecture with enhanced performance. By fabricating Au and Pd gratings on a p-type Si substrate, >1 A/W responsivities were obtained at the relatively low biases of 275 and 93 mV, respectively, with the minimum noise equivalent power <10 pW/Hz in each case. This performance brings plasmonic, near-infrared, Si-based photodetectors nearly comparable to commercially available, non-Si-based, near-infrared photodetectors.

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Publication Location:

Article Title: prDeep: Robust Phase Retrieval with a Flexible Deep Network

Authors: Christopher A. Metzler, Philip Schniter, Ashok Veeraraghavan, Richard G. Baraniuk

Keywords: Phase retrieval algorithms, imaging

Abstract: Phase retrieval algorithms have become an important component in many modern computational imaging systems. For instance, in the context of ptychography and speckle correlation imaging, they enable imaging past the diffraction limit and through scattering media, respectively. Unfortunately, traditional phase retrieval algorithms struggle in the presence of noise. Progress has been made recently on developing more robust algorithms using signal priors, but at the expense of limiting the range of supported measurement models (e.g., to Gaussian or coded diffraction patterns). In this work we leverage the regularization-by-denoising framework and a convolutional neural network denoiser to create prDeep, a new phase retrieval algorithm that is both robust and broadly applicable. We test and validate prDeep in simulation to demonstrate that it is robust to noise and can handle a variety of system models.

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Date Submitted: 5/20/19 12:00AM

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Publication Location:

Article Title: Ligand-Dependent Colloidal Stability Controls the Growth of Aluminum Nanocrystals

Authors: Benjamin D. Clark, Christopher J. DeSantis, Gang Wu, David Renard, Michael J. McClain, Luca Bursi, A

Keywords: Aluminum Nanocrystals, EPR, size and shape control

Abstract: The precise size- and shape-controlled synthesis of monodisperse Al nanocrystals remains an open challenge. Here we pursue a molecular-level understanding of the formation of Al nanocrystals by titanium(IV) isopropoxide-catalyzed decomposition of AlH₃ in Lewis base solvents. As determined by EPR spectroscopy of intermediates, the reaction begins with the formation of Ti³⁺-AlH₃ complexes. Proton nuclear MR spectroscopy indicates isopropoxy ligands are removed from Ti by Al, producing aluminum(III) isopropoxide and low-valent Ti³⁺ catalysts. These Ti³⁺ species catalyze elimination of H₂ from AlH₃ inducing the polymerization of AlH₃ into colloiddally unstable low-valent aluminum hydride clusters. These clusters coalesce and grow while expelling H₂ to form colloiddally stable Al nanocrystals. The colloidal stability of the Al nanocrystals and their size is determined by the molecular structure and density of coordinating atoms in the reaction, which is controlled by choice of solvent composition.

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Publication Location:

Article Title: Polydopamine-Stabilized Aluminum Nanocrystals: Aqueous Stability and Benzo[a]pyrene Detection

Authors: David Renard, Shu Tian, Arash Ahmadvand, Christopher J. DeSantis, Benjamin D. Clark, Peter Nordlar

Keywords: aluminum, nanoparticles, polydopamine, H₂O stability, SERS detection

Abstract: Aluminum nanocrystals have emerged as an earth abundant material for plasmonics applications. Al nanocrystals readily oxidize in aqueous-based solutions, however, transforming into highly stratified γ -AlOOH nanoparticles with a 700% increase in surface area in a matter of minutes. Here we show that by functionalizing Al nanocrystals with the bioinspired polymer polydopamine, their stability in aqueous media is dramatically increased, maintaining their integrity in aqueous solution for over 2 weeks with no discernible structural changes. Polydopamine functionalization also provides a molecular capture layer that enables the capture of polycyclic aromatic hydrocarbon pollutants in H₂O samples and their detection by surface-enhanced Raman spectroscopy, when polydopamine-stabilized Al nanocrystal aggregates are used as substrates. This approach was used to detect a prime carcinogenic H₂O pollutant, benzo[a]pyrene with a sensitivity in the sub part-per-billion range.

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Publication Location:

Article Title: Inverse Scattering via Transmission Matrices: Broadband Illumination and Fast Phase Retrieval Algorithms

Authors: Manoj Kumar Sharma, Christopher A. Metzler, Sudarshan Nagesh, Richard G. Baraniuk, Oliver Cossair

Keywords: Transmission Matrix, Phase Retrieval, Scattering.

Abstract: When a narrowband coherent wavefront passes through or reflects off of a scattering medium, the input and output relationship of the incident field is linear and so can be described by a transmission matrix (TM). If the TM for a given scattering medium is known, one can computationally "invert" the scattering process and image through the medium. In this paper, we investigate the effect of broadband illumination, i.e., what happens when the wavefront is only partially coherent? Can one still measure a TM and "invert" the scattering? To accomplish this task, we measure TMs using the double-phase retrieval technique, a method that uses phase retrieval algorithms to avoid difficult-to-capture interferometric measurements. Generally, using the double-phase retrieval method requires performing massive amounts of computation. We alleviate this burden by developing a fast, GPUaccelerated algorithm, prVAMP, which lets us reconstruct 2562×642 TMs in under five hours.

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Date Submitted: 10/30/20 12:00AM

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Publication Location:

Article Title: Aluminum Nanocrystals Grow into Distinct Branched Aluminum Nanowire Morphologies

Authors: Benjamin D. Clark, Minhan Lou, Peter Nordlander, and Naomi J. Halas

Keywords: plasmonics, waveguides, nanophotonics, oriented attachment, self-assembly

Abstract: Plasmonic nanowires (NWs) have generated great interest in their applications in nanophotonics and nanotechnology. Here we report the synthesis of Al nanocrystals (NCs) with controlled morphologies that range from nanospheres to branched NW and NW bundles. This is accomplished by catalyzing the pyrolysis of triisobutyl aluminum (TIBA) with Tebbe's reagent, a titanium(III) catalyst with two cyclopentadienyl ligands. The ratio of TIBA to Tebbe's reagent is critical in determining the morphology of the resulting Al NC. The branched Al NWs grow in their $\{100\}$ directions and are formed by oriented attachment of isotropic Al NCs on their $\{100\}$ facets. Branched NWs are strongly absorptive from the UV to the mid-IR, with longitudinal dipolar, higher-order, and transverse plasmons, all contributing to their broadband response. This rapid Al NW synthesis enables the expanded use of Al for plasmonic and nanophotonic applications in the ultraviolet, visible, and infrared regions of the spectrum.

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Date Submitted: 10/30/20 12:00AM

Date Published: 8/9/19 7:58PM

Publication Location:

Article Title: Aluminum Nanocubes Have Sharp Corners

Authors: Benjamin D. Clark, Christian R. Jacobson, Minhan Lou, David Renard, Gang Wu, Luca Bursi, Arzeena S

Keywords: shape control, plasmonics, field-enhancement, {100} faceted, nanotechnology

Abstract: Of the many plasmonic nanoparticle geometries that have been synthesized, nanocubes have been of particular interest for creating nanocavities, facilitating plasmon coupling, and enhancing phenomena dependent upon local electromagnetic fields. Here we report the straightforward colloidal synthesis of single-crystalline {100} terminated Al nanocubes by decomposing AlH₃ with Tebbe's reagent in tetrahydrofuran. The size and shape of the Al nanocubes is controlled by the reaction time and the ratio of AlH₃ to Tebbe's reagent, which, together with reaction temperature, establish kinetic control over Al nanocube growth. Al nanocubes possess strong localized field enhancements at their sharp corners and resonances highly amenable to coupling with metallic substrates. Their native oxide surface renders them extremely air stable. Chemically synthesized Al nanocubes provide an earth-abundant alternative to noble metal nanocubes for plasmonics and nanophotonics applications.

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Publication Location:

Article Title: Shining Light on Aluminum Nanoparticle Synthesis

Authors: Christian R. Jacobson*, David Solti*, David Renard, Lin Yuan, Minghe Lou, and Naomi J. Halas

Keywords: Shape Control, Plasmonic nanoparticles, Aluminum nanocrystals

Abstract: The chemical synthesis of Al nanocrystals (NCs) of controlled size and shape has historically lagged far behind that of Au and Ag. This is partially due to the high reactivity of Al precursors, which react readily with O₂, H₂O, and many reagents used in traditional NC syntheses. The first chemical synthesis of Al NCs was demonstrated in 1998, decomposing AlH₃ using titanium isopropoxide (TIP), with a number of subsequent reports refining this protocol. The role of a catalyst in Al NC synthesis is, we believe, unique to this synthetic approach. In 2015, the first synthesis of size controlled Al NCs was published by our group. Since then, we have significantly advanced Al NC synthesis, postsynthetic modifications, and applications of Al nanoparticles (NPs)? NCs with additional surface modifications?in chemical sensing and photocatalysis. Colloidal Al synthesis has its unique challenges, differing markedly from the far more familiar Au and Ag syntheses, which currently appears to present

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CONFERENCE PAPERS:

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Date Received: 23-Oct-2017

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Conference Location: Stanford, CA, USA

Paper Title: Coherent inverse scattering via transmission matrices: Efficient phase retrieval algorithms and a public dataset

Authors: C. Metzler, M. Sharma, S. Nagesh, R. Baraniuk, O. Cossairt, A. Veeraraghavan

Acknowledged Federal Support: Y

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DISSERTATIONS:

Publication Type: Thesis or Dissertation

Institution: Rice University

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Title: Imaging through opaque media and photodetection using engineered nanostructures

Authors: Mehbuba Tanzid

Acknowledged Federal Support: **Y**

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Institution: Rice University

Date Received: 20-May-2019

Completion Date: 5/5/19 4:17PM

Title: The Best of Both Worlds: Antenna-Reactor Nanomaterials for Plasmonic Photocatalysis

Authors: Dayne Francis Swearer

Acknowledged Federal Support: **N**

Partners

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I certify that the information in the report is complete and accurate:

Signature: Surbhi Lal

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GOALS

The MURI: Coherent Effects in Hybrid Nanostructures for Lineshape Engineering of Electromagnetic Media was started with the on the following goals:

- ***to understand, design, and optimize standalone nanoparticles and their assemblies*** for transparency windows at specific frequencies;
- ***collaborative studies on morphologies*** resulting in tailored spectral transparency windows;
- ***to develop new, low-loss, lower-cost, benign, metallic and semiconductor nanoparticles*** and nanocomplexes to realize these effects;
- ***to perform optical measurements*** from the **visible to the far-IR** regions of the spectrum, to characterize and optimize engineered linewidths in these systems;
- ***to advance the surface chemistry*** of nanoassemblies, facilitating **fluid or vapor phase particle dispersal** for evaluation of particulate optical properties.

As the MURI progressed, we focused the nanocrystal synthesis to aluminum-based nanocrystals and their modifications and developed algorithms and techniques to image through scattering media.

- **Ligand-directed growth of Al reduced-symmetry NCs**, to extend Al NC resonances into and across the infrared region of the spectrum;
- **Catalyst variation for controlled-aspect-ratio Al NC nanorods** and large-aspect-ratio nanowires, to examine the long-wavelength properties and capabilities of large aspect-ratio nanorods;
- **Seed-mediated growth by Ag nanostructures**: exploiting the lattice-matching between Ag and Al to synthesize reduced-symmetry Al nanostructures such as nanoplates (in collaboration with Nanocomposix);
- **H₂O-based separation procedures for coated Al NC and NRs**, critical for all chemically synthesized Al nanoparticle, enabled by our coatings developed in the last funding cycle;
- **Incorporation of new materials for added functionality and stability**: Ti doping of Al NCs (TiAl cores); Al-doped TiO₂ coating layers; growth of TiN coatings around Al NCs for added infrared capabilities along with high-temperature durability
- **Imaging through scattering media**

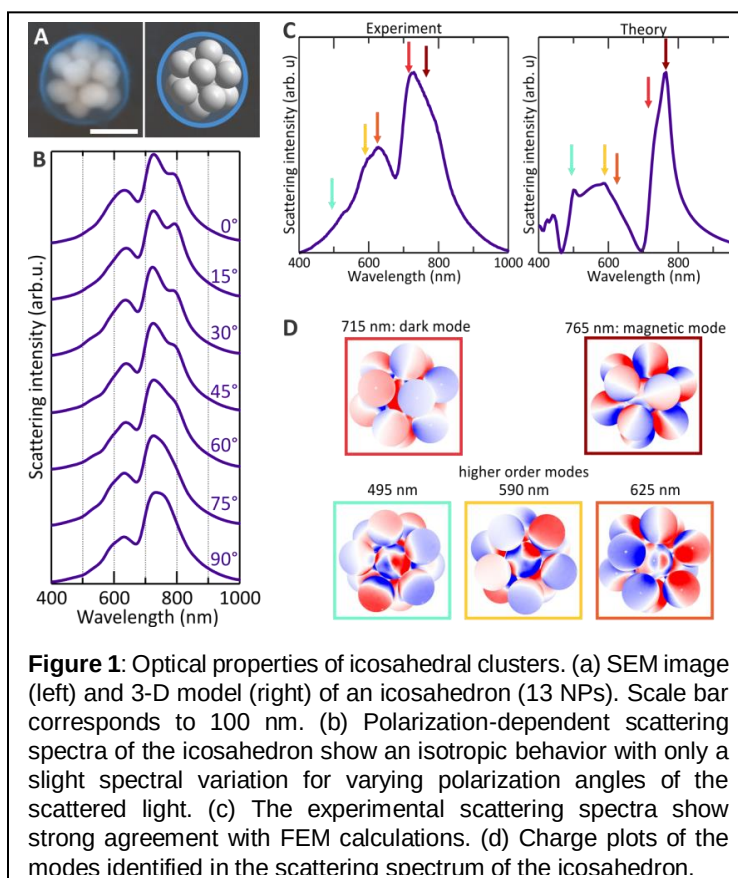
SCIENTIFIC ACCOMPLISHMENTS:

The overarching theme of the MURI project was to develop 3D structures with tailored lineshapes and transparency windows. To accomplish this we started with designing multilayer particles, and clusters of particles and self similar particles to tune the resonances and achieve lineshapes with a transparency window.

Optical Properties of Nanoparticle Clusters

Assembling nanoparticles into well-defined structures is an important way to create and tailor the optical properties of materials. We have developed an efficient method for assembling noble metal nanoparticles into stable, three-dimensional clusters, whose optical properties can be highly sensitive or remarkably independent of cluster orientation, depending on particle number and cluster geometry.

Clusters with highly orientation-independent optical properties, such as tetrahedra and icosahedra, could enable polarization-independent and non-directional negative index media like fluids, free-form solids and isotropic films. The universality of the fabrication method reported here can extend the use of plasmonic nanoclusters to other regions of the spectrum by incorporating either different materials, e.g. Aluminum for the UV, or spherical core/shell nanoparticles, e.g., nanoshells for the IR. These nanostructures exhibit multiple Fano resonances and an isotropic optical response. By tuning the nanoparticle size and interparticle spacings, the Fano resonances and their transparency windows can be tuned across the visible and near IR. This project is a collaboration between the Halas and Nordlander groups. (Urban et al. Nanoletters 2013)



Fractal Nanostructure Plasmonics

We are investigating the plasmonic properties of fractal nanostructures, and our study of these structures is motivated by the observed broadband absorbance and scattering capabilities of wet chemically synthesized gold fractal-like particles. To better understand these more complex systems, we have begun studying the plasmonic properties of a fundamental fractal system, the Cayley tree. Fourier Transform Infrared Spectroscopy has been used to investigate the plasmonic

modes of a 2D arrays of the symmetric $N = 1$, $N = 2$, and $N = 3$ Cayley trees ($N = \#$ of iterations). The large area arrays of the structures have been fabricated using high precision e-beam lithography on quartz substrates. We have measured the transmittance of unpolarized light through these three structures, and characterized the structures through Scanning Electron Microscopy (SEM) (Fig.2). As seen in Figure 2, as the number of structural iterations increases we see an increasing number of

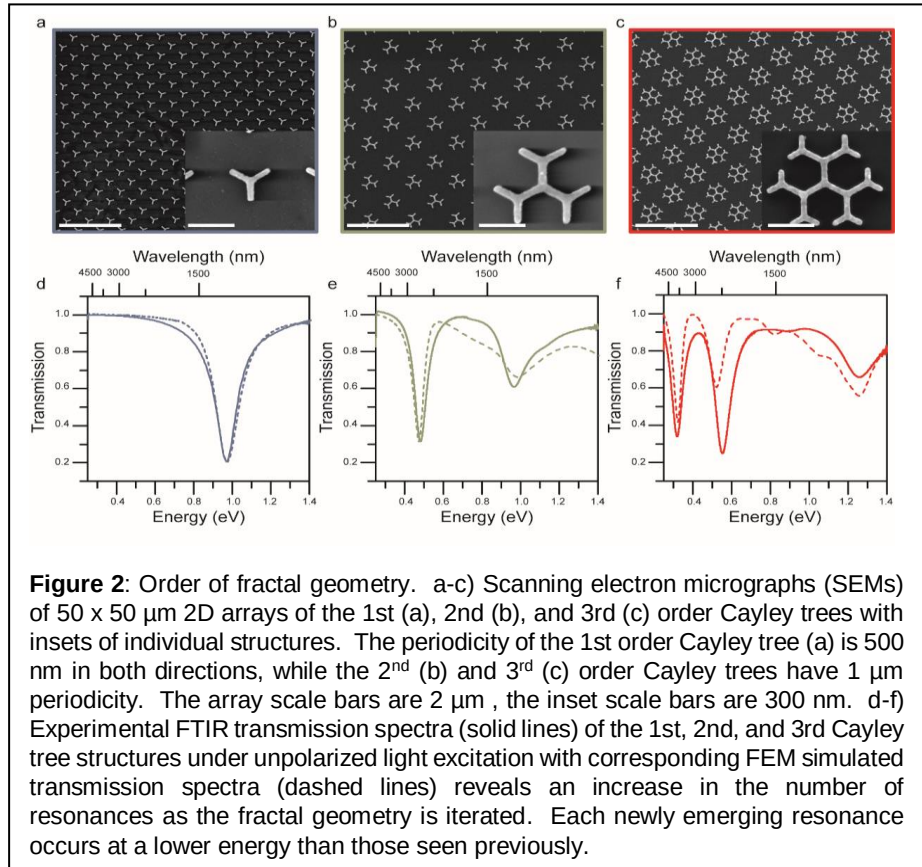


Figure 2: Order of fractal geometry. a-c) Scanning electron micrographs (SEMs) of 50 x 50 μm 2D arrays of the 1st (a), 2nd (b), and 3rd (c) order Cayley trees with insets of individual structures. The periodicity of the 1st order Cayley tree (a) is 500 nm in both directions, while the 2nd (b) and 3rd (c) order Cayley trees have 1 μm periodicity. The array scale bars are 2 μm , the inset scale bars are 300 nm. d-f) Experimental FTIR transmission spectra (solid lines) of the 1st, 2nd, and 3rd Cayley tree structures under unpolarized light excitation with corresponding FEM simulated transmission spectra (dashed lines) reveals an increase in the number of resonances as the fractal geometry is iterated. Each newly emerging resonance occurs at a lower energy than those seen previously.

modes. In order to better model more complex systems we have investigated higher order Cayley Trees and Cayley Trees with non-uniform leg lengths. We have investigated the tunability of these plasmons by varying leg lengths and widths, as well as by changing their aspect ratio. The extinction spectra of fractals show broad spectra with several peaks and minima that can be used to design optical materials with peculiar transmission properties. Theoretical simulations were performed in collaboration with Dr. Govorov's group and show excellent agreement with the FTIR spectra for the different iterations of the nanostructure and also the variations of varying leg lengths and widths. The modes can now be understood as intra-arm, inter-arm and global plasmonic modes. To elucidate the nature of the modes, charge distribution and field maps were calculated. (Gottheim et al. 2015).

Nanoparticle - Dye Plexitonic nanocomplexes

Metallic nanoparticles exhibiting plasmonic Fano resonances can provide large enhancements of their internal electric near field. Here we show that

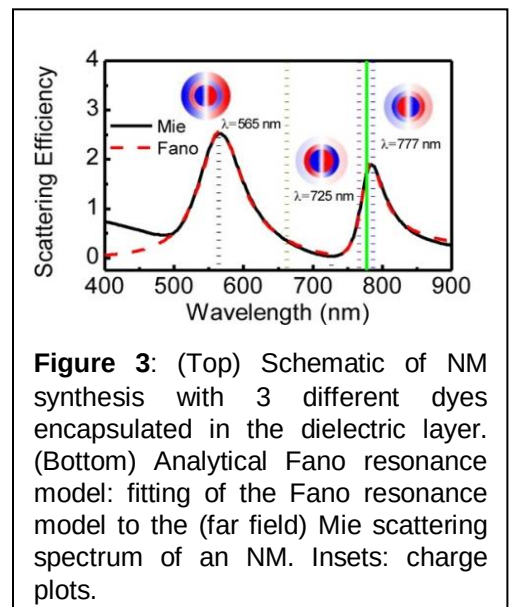
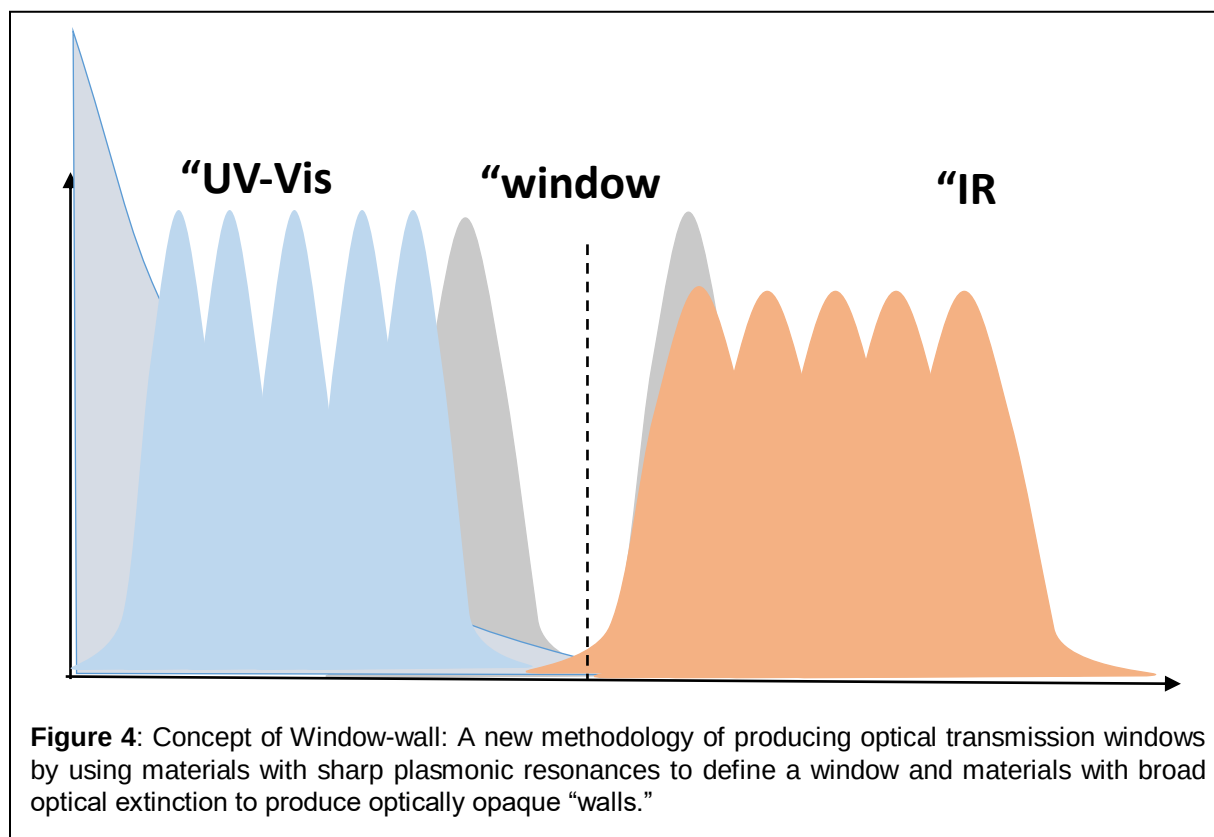


Figure 3: (Top) Schematic of NM synthesis with 3 different dyes encapsulated in the dielectric layer. (Bottom) Analytical Fano resonance model: fitting of the Fano resonance model to the (far field) Mie scattering spectrum of an NM. Insets: charge plots.

nanomatrixoshkas, nanoparticles consisting of an Au core, an interstitial nanoscale SiO₂ layer, and an Au shell layer, can selectively provide either a strong enhancement or a quenching of the spontaneous emission of fluorophores dispersed within their internal dielectric layer. The plasmonic properties result from the strong interaction between the plasmon modes of the Au core and the Au shell, giving rise to hybridized modes that can be tuned into the NIR, for particle sizes below 100 nm in diameter. These interactions also give rise to a strong Fano resonance in the visible region of the spectrum, appearing as an asymmetric modulation in the far-field extinction spectrum of the nanoparticle. This modulation of the fluorescence can be understood by taking into account the near-field enhancement induced by the Fano resonance of the nanomatrixoshka, which is responsible for enhanced absorption of the fluorophores incorporated into the nanocomplex. The combination of compact size and enhanced light emission with internal encapsulation of the fluorophores increases the biocompatibility of these nanoparticles and makes them safe for large scale use.

The above demonstrates techniques developed to encapsulate dye molecules in the silica layer – the region of the largest field enhancement in the nanoparticle. Currently we are investigating the encapsulation of NIR dyes that form J-aggregates into the nanomatrixoshka nanoparticles. (Ayala et al. Nanoletters 2014)

Wall-Window Concept



In a collaborative project with Professors Hogan and Govorov, Kortshagen’s group demonstrated a new methodology of producing optical transmission windows by using materials with sharp

plasmonic resonances to define a window and materials with broad optical extinction to produce optically opaque “walls.” The first demonstration was based on solutions of plasmonic gold and excitonic semiconductor NCs. In this materials system, the plasmonic gold nanorods are used to define the narrow transmission window. Figure 5 shows transmission spectra of various solutions of gold nanorods that are used to define a transmission window at 700 nm. Due to the narrow absorption of the gold nanorods, there is remaining transmission in the blue and infrared range. The blue transmission was canceled by the addition of colloidal B-doped Si NCs synthesized with the nonthermal plasma technique. B-doping leads to highly-dispersive Si NCs with excellent transparency in the visible-to-near IR spectral range and a high extinction coefficient in the shorter-wavelength region, demonstrating an efficient wall material for short-wavelength light. In our demonstration, water served as the near IR “wall” material. As shown in Figure 4, narrow transmission windows were obtained with a broad extinction spectral range of 200 nm to 3300 nm (instrument limits) and tailored window properties.

Theoretically we have explored the limits, numerically, of both diluted and dense collections of plasmonic nanorods and observed the limits of the applicability of the Beer’s law. The Beer’s law, which is applicable for weakly-interacting nanoparticles, works generally very well and becomes broken only when nanorods are nearly touching. In particular, we observed that the aggregated nanorods violate the Beer’s law and the aggregation can destroy the window effect. For these simulations, we used COMSOL and a relatively large collection of randomly-oriented nanorods. (Yang 2016).

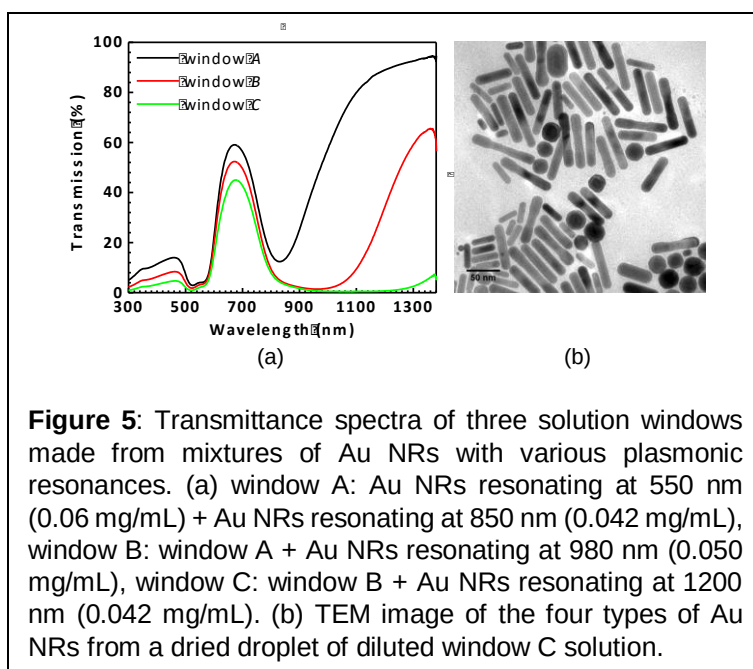
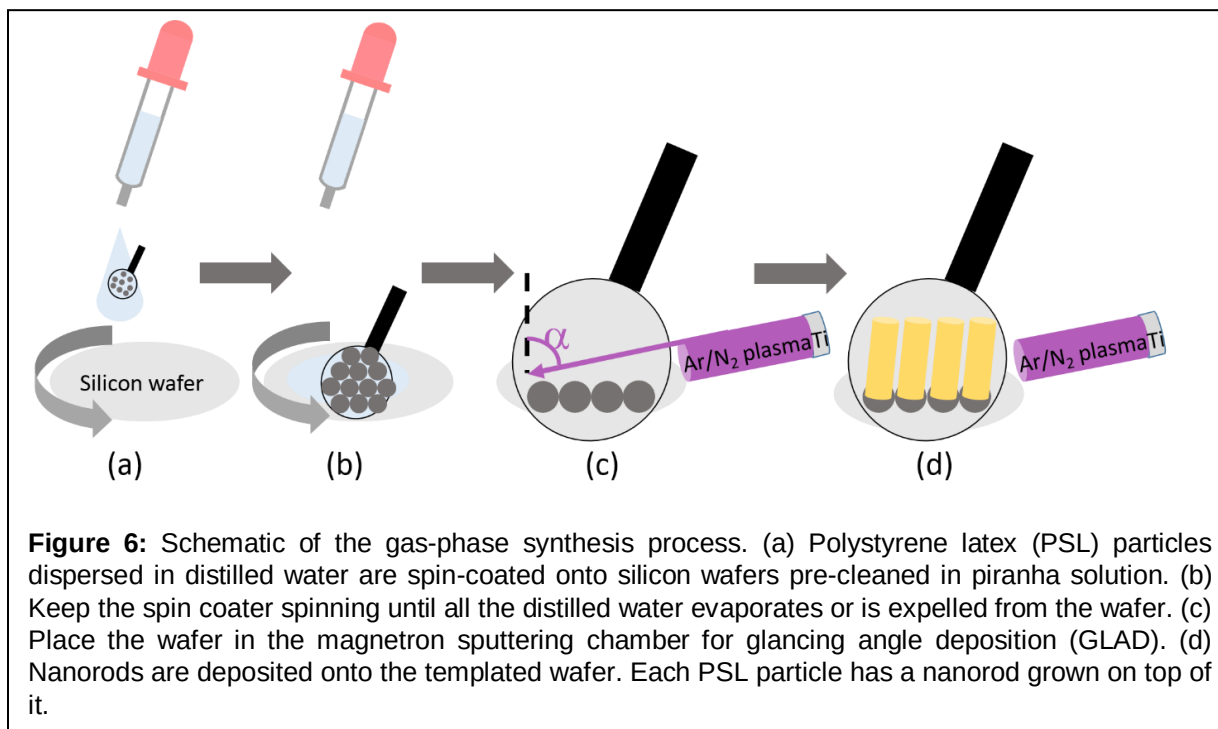


Figure 5: Transmittance spectra of three solution windows made from mixtures of Au NRs with various plasmonic resonances. (a) window A: Au NRs resonating at 550 nm (0.06 mg/mL) + Au NRs resonating at 850 nm (0.042 mg/mL), window B: window A + Au NRs resonating at 980 nm (0.050 mg/mL), window C: window B + Au NRs resonating at 1200 nm (0.042 mg/mL). (b) TEM image of the four types of Au NRs from a dried droplet of diluted window C solution.

Titanium Nitride Nanorods:

The window in the “window – wall frame” can be defined by gold nanorods or Titanium Nitride nanorods.

We developed a gas-phase synthesis method for plasmonic nanorods, namely, combining magnetron sputtering and template-assisted glancing angle deposition. The proposed method is applicable to a variety of plasmonic materials, including titanium nitride, silver, copper, etc. Figure 6 shows a schematic of the synthesis process.



Contributing to the “absorption wall” work of the entire group, the Kotov group synthesized a new type of small plasmonic particles based on WO_{3-x} ceramics. These NP dispersions are inexpensive (primary atomic content is oxygen), have a strong adsorption at 900-1100 nm, and are easily dispersible in liquids. Their plasmonic band can be tuned using different metal ions imbedded in this ceramics. They can also display a transparency window that can be “burned” by illumination with NIR laser. Other IR plasmonic materials explored were Cu_2S , Aluminum doped Zinc oxide ($\text{Al}:\text{ZnO}$) and doped Si nanocrystals. All these nanoparticles have strong IR resonances and can be mixed to form an “IR wall”.

Another nanoparticle with strong absorption that was developed with MURI support are “hedgehog nanoparticles” (HP). different methods to counteract counteract strong van der Waals and other attraction forces between particles in water or air is possible with strong corrugations. We demonstrated that dispersing particles in liquids or air is possible when the balance of attractive and repulsive forces is altered by nanoscale topography of particle surface. Microscale hedgehog particles (HPs), coated with a layer of stiff nanospikes, exhibit long-term colloidal stability in both hydrophilic and hydrophobic media. Attractive forces between such particles are markedly decreased due to small contact area of spiky non-penetrating surfaces. Entrapment of air in aqueous dispersions and long range electrostatic repulsion in organic media also contribute to colloidal stability of HPs. Realization of such dispersions makes possible preparation of a new type of obscurants and eases their aerosolization. We also developed techniques to scale up the production of these nanoparticles.

'Hedgehog' particles (HPs) possess a micro-meter sized dielectric spherical core which is densely coated with stiff, e.g., metal oxide, nanoscale spikes. This unique surface topography, resembling the appearance of a hedgehog, provides the particles with the exclusive physiochemical property to stably disperse in both polar and non-polar solvents without the necessity of changing surface chemistry. Optical extinction measurements of HP ensembles in aqueous solution indicate a broad spectral response in the visible range, however there is a dearth of fundamental knowledge about the cause of the broad optical resonance, as it can be a consequence of shape polydispersity in the many-particle system or essential to each individual HP. We therefore studied the dark-field scattering of individual HPs. Such measurements disclosed that the expansive optical response in the visible spectral range is truly characteristic for the far-field scattering of a single HP (Figure 7). Our results uncovered how intrinsic particle features, such as spike length, as well as environmental changes affect the scattering response of individual HPs. We found that the spectral resonance of a HP follows a Lorentzian lineshape, typical for a dipole scatterer. The maximum of the Lorentzian scattering profile of a HP shifts to longer wavelengths with increasing spike length. By changing the atmosphere around a hydrophilic HP from air to nitrogen, we discovered that the scattering response of the particle is primarily dominated by excess water in its interstitial shell. Additionally, we determined that a microscope glass substrate has no significant impact on the spectral response of a hydrophilic HP in water by employing a 3D optical trap that provided a homogenous environment. (Kirchner et al. 2018)

TiN Nanorods and Nanostars

We have investigated optical properties of two interesting systems, TiN nanocubes and Au nanostars. TiN nanocrystals attract now lots of interest since this material is both cheap and plasmonic. In the previous reports, we predicted high mass extinction coefficients (MECs) for non-spherical nanocrystals made of this plasmonic ceramic-like material. In this particular study, we computed optical and photocatalytic properties of TiN nanocubes and then compared the results with the traditional plasmonic Au nanocrystals. For the experiment, TiN cubes were bought from a company in Germany. We found that overall TiN nanocubes exhibit strong absorption peaks in the red and infrared. As compared to the Au nanocrystals, TiN has intensive red-shifted and strongly-broadened resonances. Simultaneously, plasmon resonances in the TiN cubes are much stronger than those in the TiN spheres (Kong 2017) .

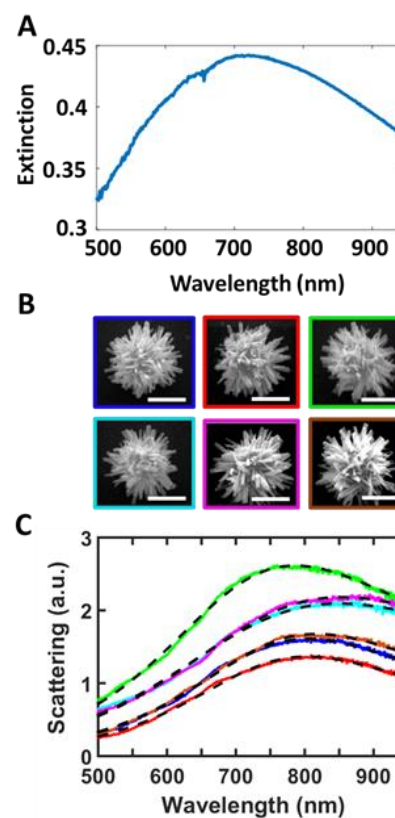


Figure 7: Hedgehog Particles (A) The ensemble extinction spectrum of hydrophilic HPs in aqueous solution shows an broad resonance in the visible-NIR region with a maximum around $\lambda = 700$ nm. (B) SEM images of individual hydrophilic HPs. Scale bar 1 μ m. (C) Single particle dark-field scattering spectra of individual hydrophilic HPs deposited on a glass substrate. The colors of the spectra match the colors of the SEM image borders in (B). The natural broadening of a HP spectrum can be fitted with a Lorentzian function (black dotted lines), characteristic for a dipole scatterer. Spectral features, such as line shape and resonance position are similar for all single HPs.

Another, very interesting type of a nanocrystal is a nanostar. Unlike plasmonic spheres, nanostars have very strong and red-shifted plasmonic peaks (Figure 8). The red shift in the plasmon peak comes together with the appearance of plasmonic hot spots at the tips (Figure 8 e). Unlike the nanorods, the nanostars exhibit nearly isotropic optical properties which can be useful for obscurants. Obscurant particles are typically randomly oriented and, therefore, strong and isotropic optical response can be useful. In addition, we looked at the rates of generation of hot electrons in these nanostars with the goal to evaluate possible usage of these nanocrystals for photocatalytic applications. (Naldoni 2017)

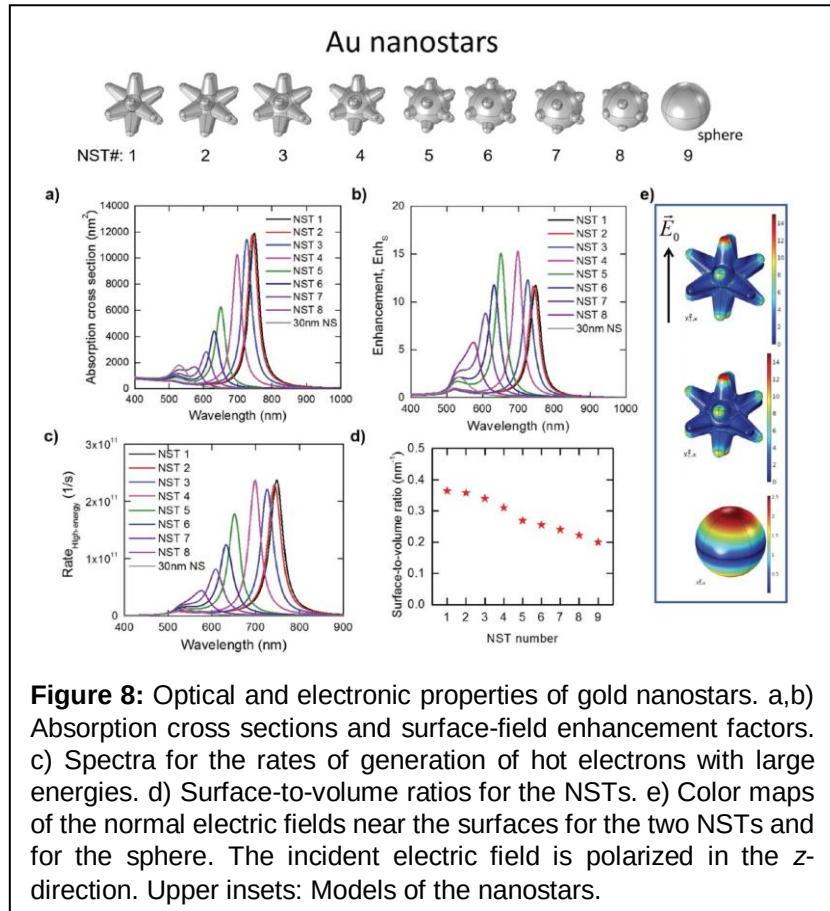


Figure 8: Optical and electronic properties of gold nanostars. a,b) Absorption cross sections and surface-field enhancement factors. c) Spectra for the rates of generation of hot electrons with large energies. d) Surface-to-volume ratios for the NSTs. e) Color maps of the normal electric fields near the surfaces for the two NSTs and for the sphere. The incident electric field is polarized in the z-direction. Upper insets: Models of the nanostars.

Tunable AZO nanocrystals

Another exciting NIR-plasmonic material is aluminum-doped zinc oxide (AZO). In preliminary studies, we found that small ($\sim 5\text{nm}$ diameter) AZO nanocrystals can be produced in a plasma. However, the NCs often do not show any LSPR. We discovered that the lack of LSPR is related to the depletion of carriers through hydroxyl related surface trap states. When the surfaces of the AZO nanocrystals were “sealed” through atomic layer deposition of alumina, strong and tunable LSPRs in AZO crystals were observed. We hypothesize that we should be able to overcome this problem by synthesizing larger AZO particles, as surface effects will be reduced for larger diameter particles.

Tunable Tungsten Oxide nanoparticles

Tungsten oxide NPs were synthesized by the controlled hydrolysis of tungsten chloride precursor in ethanol media in presence of stabilizer - aspartic acid. An aqueous solution of NaOH was added to a yellow ethanol solution of WCl_6 and incubated at room temperature under stirring for 12 h.

Subsequently the particles were centrifuged and re-dispersed either in water or ethanol to obtain a brightly blue or green-blue colored dispersion with plasmonic band at 800-1000 nm. TEM imaging revealed that WO_{3-x} NPs have a diameter of 3-20 nm. Optimization of reaction conditions allowed us to optimize the particle size and obtain stable dispersions with a uniform particle diameter of 5 nm. X-ray diffraction pattern display peaks – although broadened with a nearly perfect match to that of the structure of WO_3 .

We observed that a plasmonic band can be changed by varying the reaction conditions which is attributed to the difference of non-stoichiometric tungsten atoms in the particles. We are investigating now a possibility of illumination-induced bleaching at of the plasmonic band induced by the laser illumination. Figure 10 shows the tunable plasmonic bands in WO_{3-x} nanoparticles, and the lower panel shows the nanoparticle spectrum after illumination with a 808 nm NIR laser for 30 minutes.

Synthesis of Iron Selenide nanoparticles

Iron chalcogenides can also exhibit strong plasmonic bands. In collaboration with Halas group we are investigating their plasmonic properties. Iron Selenide nanoparticles exhibit strong –bands at 400, 1000, and 2800 nm. The bands at 100 and 2800 nm could be plasmonic which is being evaluated by A. Govorov.

We made FeSe_2 particles using the two-dimensional (2D) multistage self-assembly (SA) of ultrasmall FeSe_2 nanoparticles (NPs, ~2 nm) into ultrathin single-crystal nanosheets, having the lateral dimensions of ~600–1000 nm with the thickness of ~5.5 nm. And surprisingly, by increasing the concentration of dodecanethiol (DT) (or oleylamine (OLA)), the more complex multistage self-assembly from ultrasmall FeSe_2 NPs to mesoscale 3D nanostars are achieved. The as-prepared 3D nanostars also are of uniform size (~550 nm in the diameter), with nanoscrolls (~250 nm length, ~10–15 nm diameter, and ~2 nm wall thickness) as building blocks. Aside from

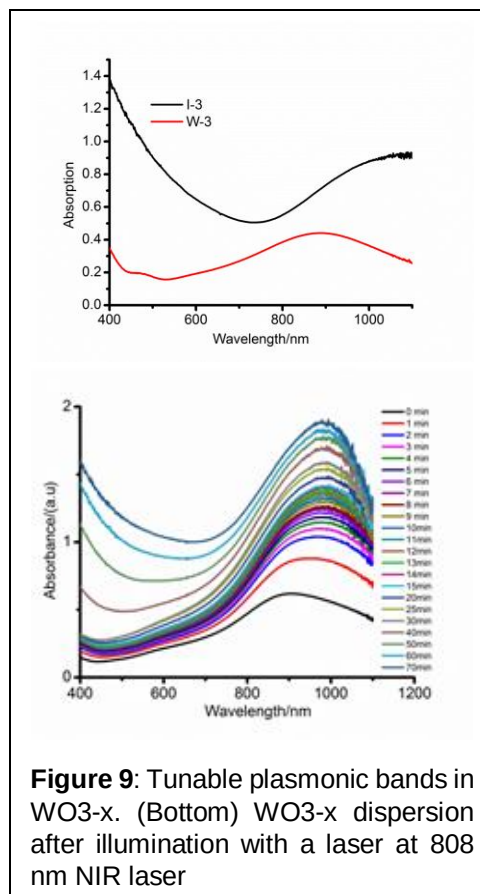


Figure 9: Tunable plasmonic bands in WO_{3-x} . (Bottom) WO_{3-x} dispersion after illumination with a laser at 808 nm NIR laser

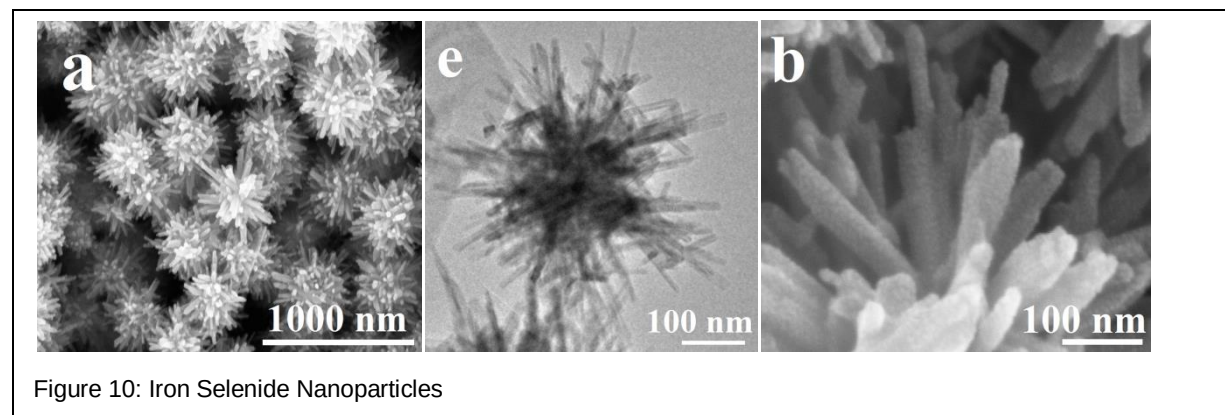


Figure 10: Iron Selenide Nanoparticles

the detailed characterizations on the size, shape and crystal structure of the as-prepared FeSe₂ nanocrystals, we also explored intensively their multistage assembly mechanisms from ultrasmall NPs.

In developing a number of nanoparticles for aerosolization as obscurants, the overall theme of developing cost effective, sustainable and non toxic materials for large volume fieldable applications. Towards this end we developed Aluminum nanocrystals of different shaped and doped Si crystals as new IR plasmonic materials.

Degenerately doped Si nanocrystals

An alternate plasmonic material with a tunable lineshape is degenerately doped Silicon nanocrystals. Si maybe doped with either Phosphorus or Boron during the growth of the Si nanocrystals in a plasma reactor. Kortshagen's group has continued to explore plasma synthesis of these doped nanocrystals.. In year 1, Kortshagen group had shown that phosphorous (P)-doped silicon nanocrystals (Si NCs) show tunable LSPRs in a range of 1,000-3,000 cm⁻¹. However, at that time, we were unable to observe any plasmonic response from boron (B)-doped Si NCs. We performed studies of the doping efficiency of P- and B-doped Si NCs and found the activation of donors and acceptors is generally weak, in the range of $\sim 10^{-2}$ - 10^{-3} , however, P and B are equally electrically active. We also observed an intriguing difference of the plasmonic response of B- and P-doped Si NCs. While P-doped Si NCs show tunable plasmonic resonances as produced, B-doped Si NCs only do so after oxidation of the Si NC surfaces has occurred (Fig. 11). This suggests that B is primarily located at the Si NC surfaces and is only activated upon oxidation of the Si NCs. This is an intriguing observation, since the oxidized B-doped Si NCs show strong LSPRs that are stable under exposure to the environment.(Gresback et al. ACS Nano 2014)

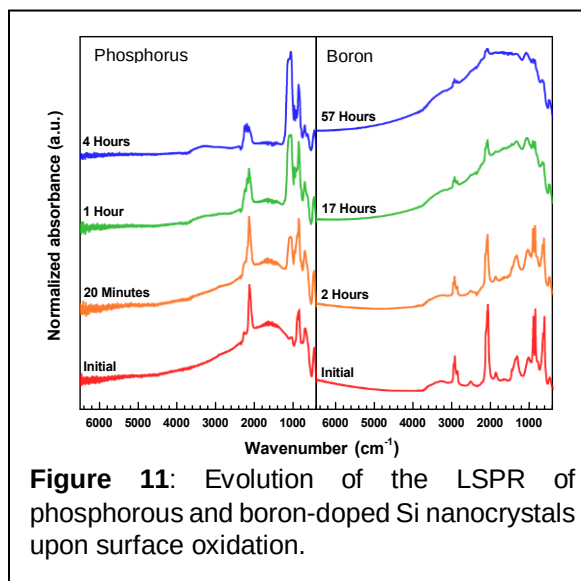
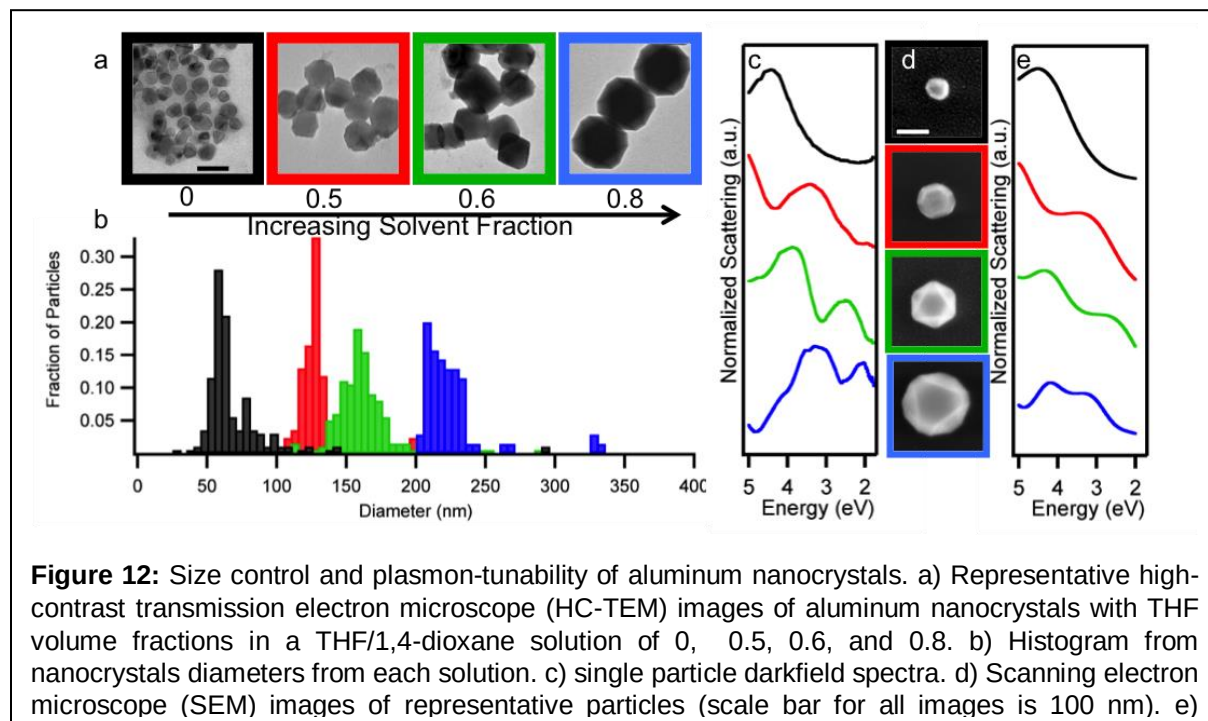


Figure 11: Evolution of the LSPR of phosphorous and boron-doped Si nanocrystals upon surface oxidation.

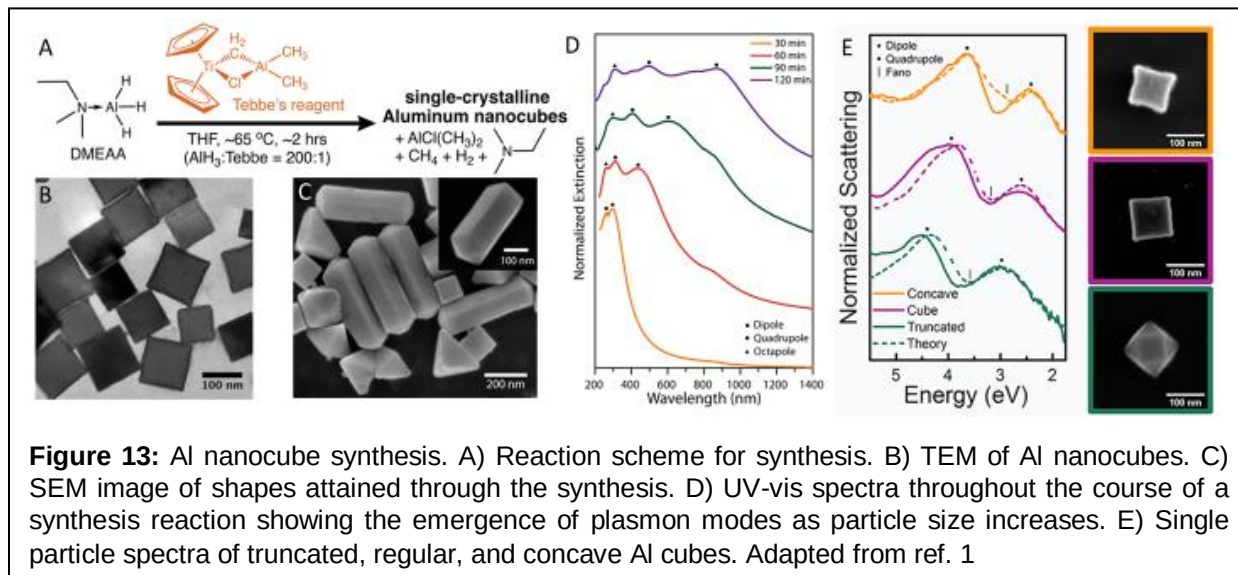
Aluminum Nanocrystals and coated nanoparticles



We have successfully synthesized aluminum nanocrystals with a large range of sizes and characterized their optical properties and composition. Another route to synthesize large volumes of aluminum nanocrystals is a wet chemistry route. We have synthesized size and shape controlled aluminum nanocrystals with tunable plasmonic properties. Aluminum nanocrystals are synthesized via thermal decomposition of dimethylethylamine alane (DMEAA) by titanium (iv) isopropoxide in the presence of oleic acid at 40°C.¹ The reaction is in a solution of tetrahydrofuran (THF) and 1,4-dioxane. By changing the ratio of THF to 1,4-dioxane, we can control the size of the particles. In a solution of only 1,4-dioxane, particles are approximately 60 nm in diameter (Figure 12a). Increasing the amount of the THF can make particles greater than 200 nm with less than 20% standard deviation in size (Figure 12b). The particles are highly crystalline, largely icosahedra and truncated trigonal bipyramids. (McClain 2015)

Al Nanocubes

When dimethylethylamine alane (DMEAA) is decomposed using Tebbe's reagent (or any of several related dicyclopentadienyl Ti or V compounds), {100}-faceted Al nanoparticles are



produced.¹ (Figure 13A, 13B) The synthesis produces on average 65 % single-crystalline nanocubes, 20 % singly-twinned bipyramids, and a small portion of penta-twinned nanorods. Nanoparticle size is tuned with reaction temperature, with cube edge lengths ranging from 50 nm to 150 nm. (Figure 13C)

Additionally, nanoparticle shape can be tuned by controlling the Al:Ti ratio in the synthesis. By varying the Al:Ti ratio between 500:1 and 50:1, the nanoparticle shape can be tuned from truncated cubes to standard cubes and then to concave cubes at the highest amount of Ti. The synthesis of these concave nanocubes indicates that shape control using Tebbe's reagent is a kinetic process, inducing Al to preferentially grow onto {111} facets to produce the cubic shape.

The optical properties of the particles were studied by UV-vis spectroscopy and by single particle dark-field scattering measurements. The dipole resonance of the particle solutions could be tuned from 300 nm with the smallest particles up to 850 nm with the largest – the resonance can be tuned across the entire visible region and into both the UV and the IR regions. (Figure 11D) Single particle spectroscopy and accompanying FDTD simulations showed that the cubes possess distinct Fano resonances, interference modes that have useful sensing applications. (Figure 11E) Additionally, electric field calculations show that the nanocubes produce approximately twice the electric field enhancement under excitation as a similarly sized sphere, while the concave cubes provide almost twice as strong enhancements as the normal cubes. Plasmonic nanocubes placed on metal films have been heavily studied as well with gold and silver, as the flat facets allow for significant coupling with the surface to produce highly sensitive resonance modes. As a proof of concept, Al nanocubes were measured on a flat gold film to show the development of these same modes.

This work is the first demonstration of Al nanocubes, with separately tunable particle size and morphology, as well as the first demonstration of particle shape control based on catalyst choice.

This method has significant promise for further Al shape tunability, providing a unique synthetic pathway unlike any other metal nanoparticle synthesis.

Al Octopods

Al octopods, a structure with six concave faces and eight protruding corners, were synthesized by further study of Tebbe's reagent as a tool for Al shape control. Rather than Al cubes, Al octopods can be easily produced by changing the reaction solvent from THF to diethylene glycol dimethyl ether and the reaction temperature from 70 °C to 110 °C. Single-crystalline particles are the major product, with ~20 % singly-twinned particles and a small proportion of penta-twinned rods. The particle size can be tuned *via* reaction temperature, yielding smaller particles at higher temperatures and allowing for dipole resonances to span the visible and UV spectral regions. This work extends the capabilities of Al shape control, demonstrating the utility of temperature and reaction solvent as additional methods of tuning the catalyst-based control scheme.

Single particle scattering measurements show that the octopods possess similar optical spectra and plasmonic modes as nanocubes, but red-shifted slightly due to the pointed corners. The similar optical spectra show that with this system, the shape and resonance energy can be tuned independently for tailored applications. The sharply pointed corners of the octopods yield stronger light focusing at the tips and higher electric field enhancements compared to spherical or cubic particles. FDTD calculations show that the octopods produce approximately 2x higher field enhancements at the corners than normal cubes and 4x stronger than spherical nanoparticles. These high field enhancements are extremely useful for applications such as enhanced sensing and photocatalysis. (Yuan 2020)

Sub-70 nm Al Nanocubes

When titanium isopropoxide ($\text{Ti}(\text{O}^i\text{Pr})_4$, TIP) and Tebbe's reagent are heated together and then mixed with an alane precursor for Al nanoparticle synthesis, small (30 – 60 nm) {100}-faceted Al nanoparticles are produced (Figure 15A, 15B). This result is in stark contrast to using either catalyst separately, indicating the formation of a previously unknown catalyst for Al nanoparticle

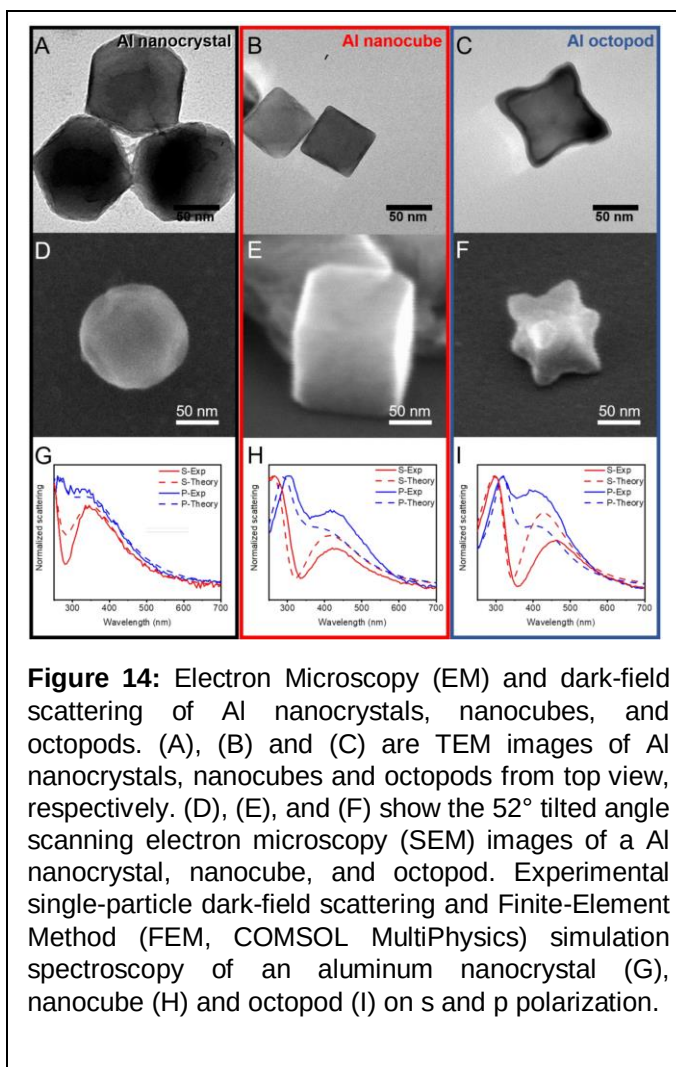
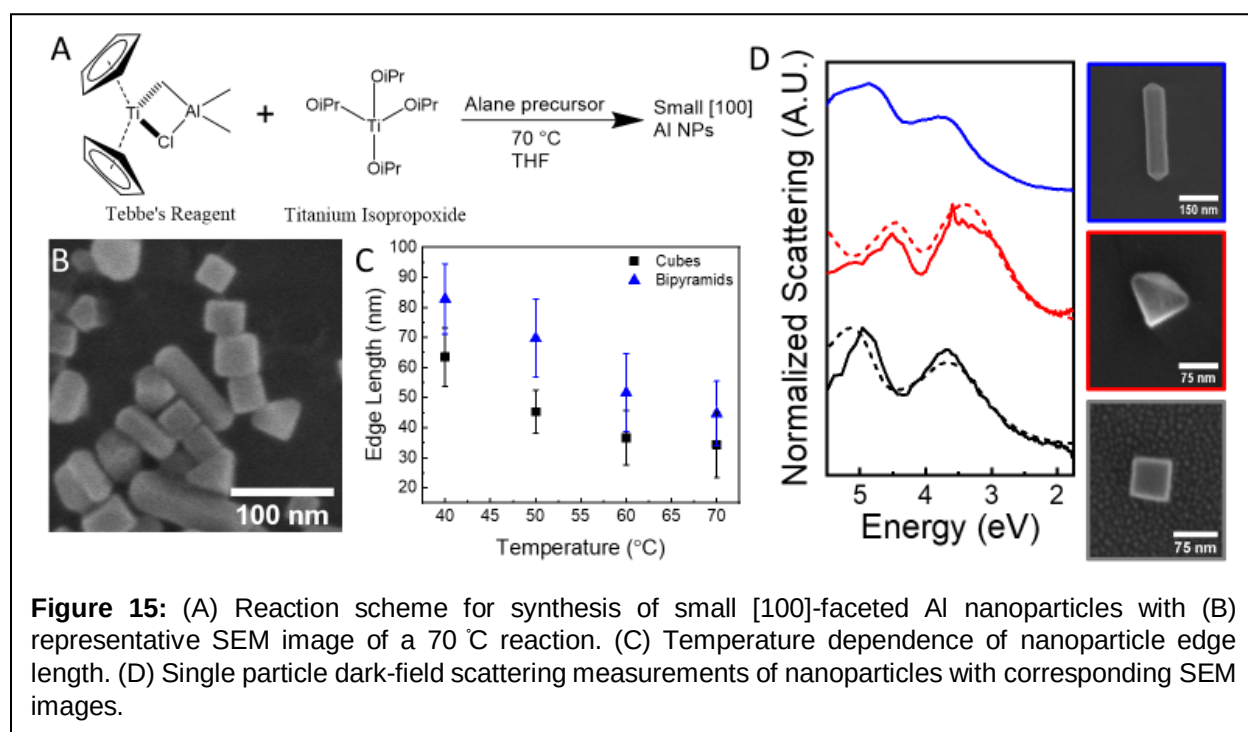


Figure 14: Electron Microscopy (EM) and dark-field scattering of Al nanocrystals, nanocubes, and octopods. (A), (B) and (C) are TEM images of Al nanocrystals, nanocubes and octopods from top view, respectively. (D), (E), and (F) show the 52° tilted angle scanning electron microscopy (SEM) images of a Al nanocrystal, nanocube, and octopod. Experimental single-particle dark-field scattering and Finite-Element Method (FEM, COMSOL MultiPhysics) simulation spectroscopy of an aluminum nanocrystal (G), nanocube (H) and octopod (I) on s and p polarization.

growth. This reaction is tunable with temperature, ranging from 65 nm cubes at 40 °C to 35 nm cubes at 70 °C. (Figure 15C) Previously, Al nanocube synthesis was only tunable to particles ~60 nm, however, this new reaction extends the attainable range of Al nanocubes and extends their LSPR deeper into the UV.

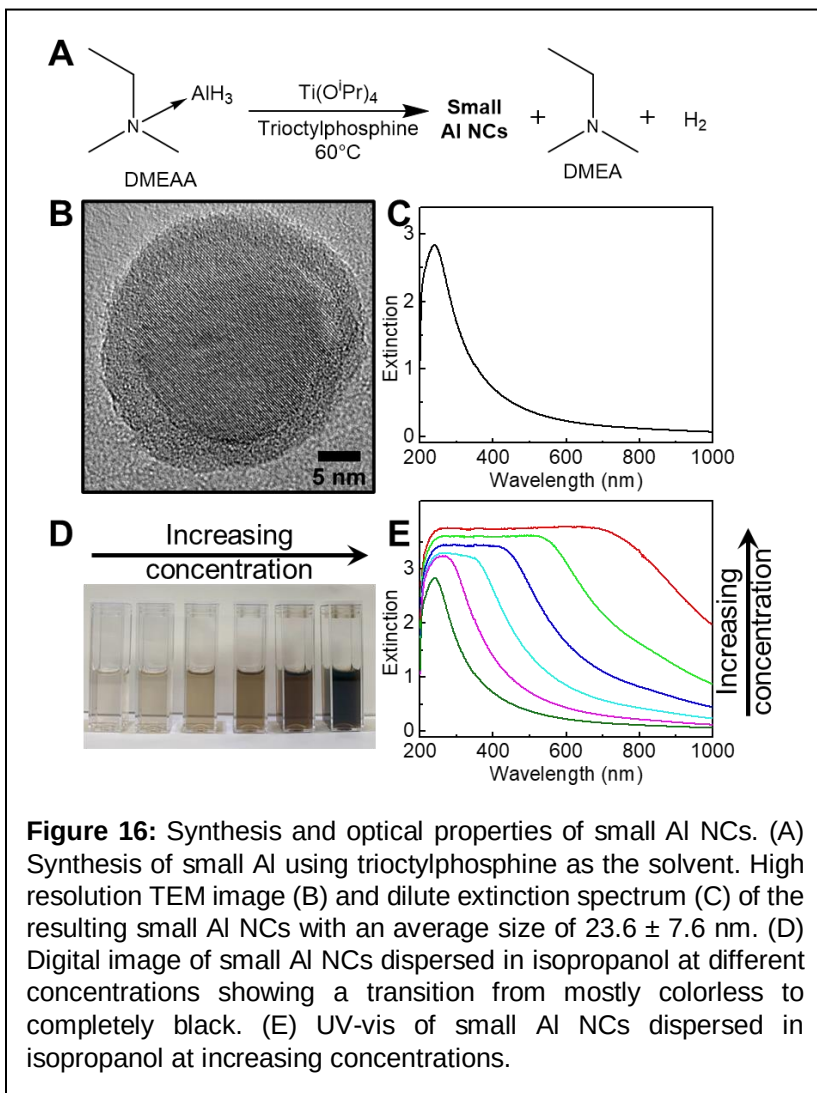
While the smallest particles obtained with this synthesis are too strongly absorbing for single particle scattering measurements, the larger particles have been studied. The cubes display similar Fano resonances as was observed with the larger cubes, while strong polarization dependence was seen with the rods. The singly twinned particles show significant orientation and polarization dependence, which is being further investigated.(Clark 2019)

The identity of the active catalyst in this reaction is under active investigation, but preliminary work indicates it is an oxygen-bridged di-titanium species, with one biscyclopentadienyl and one isopropoxide center. This research points to interesting new chemistry and an unexplored class of compounds for catalyzing Al nanoparticle growth, potentially allowing for greater shape control than has so far been achieved.



Sub-40 nm Al Nanospheres

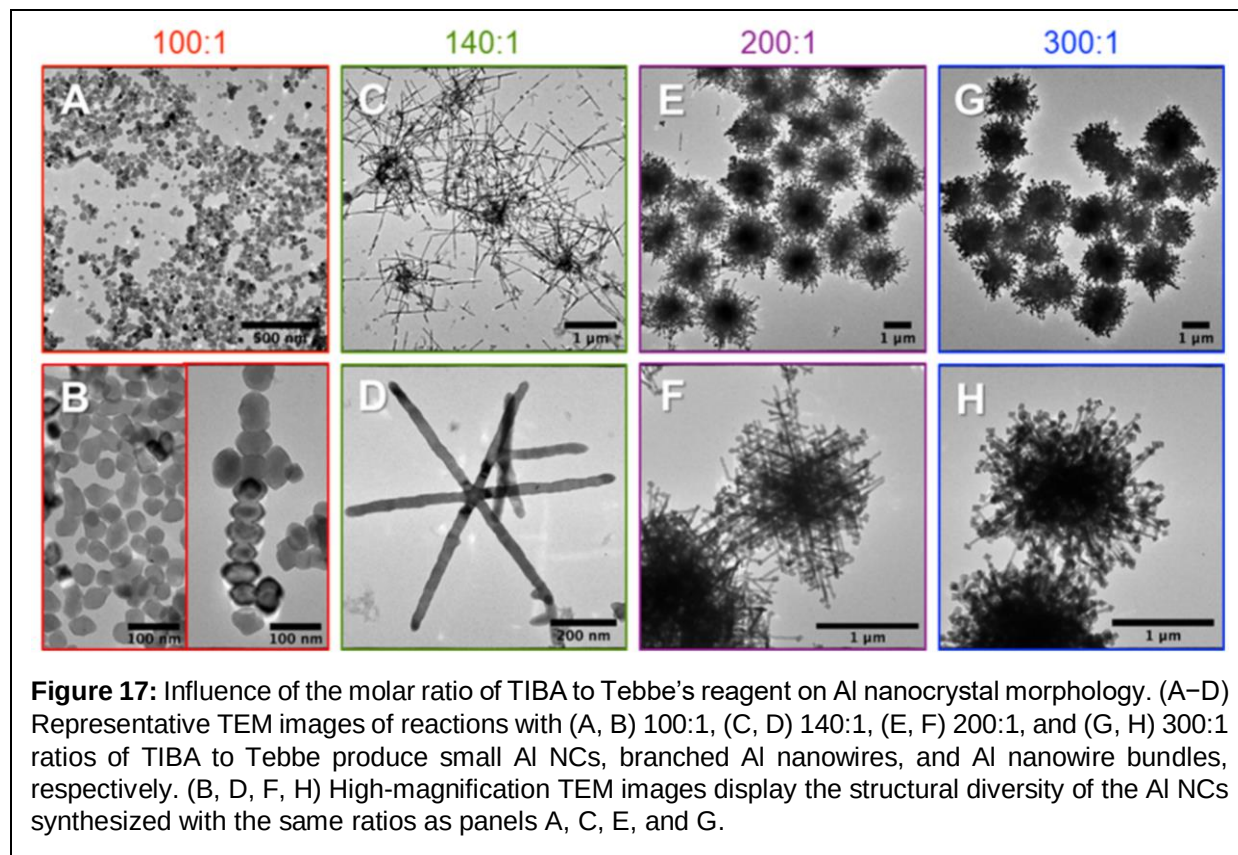
The synthesis of sub-40nm, spherical Al NPs was developed by substituting trioctylphosphine as the reaction solvent in the Ti(IV)-catalyzed decomposition of dimethylethylamine alane (DMEAA) (Figure 16A). It has been shown that phosphorus adducts of alane are more thermally reactive, decomposing readily at relative low temperatures compared to their amine analogues. We speculate that the weak Lewis base character of the phosphorus atom yields weakly coordinated alane molecules that decompose very quickly at low temperatures resulting in sub-40 nm particles (Figure 16B). We also attribute the weak affinity of trioctylphosphine to the lack of shape direction during the growth leading to the formation of quasi-spherical particles. This relatively mild synthesis is a facile method to produce small Al NPs that display a UV plasmonic response around 230 nm when dilute. Interestingly, when concentrated, the optical spectra saturate the detector and eventually completely obscure the entire visible spectrum (Figure 16C). This effect can be explained by the absorbing character of the interband transition located around 800 nm. As the sample concentration is increased, the visible absorption plays a larger role, eventually resulting in almost pure absorption across the entire visible spectrum. These small Al NPs may prove useful for photothermal heating applications due to their low cost and high absorptivity in the visible and near infrared.



Branched Al Nanowires

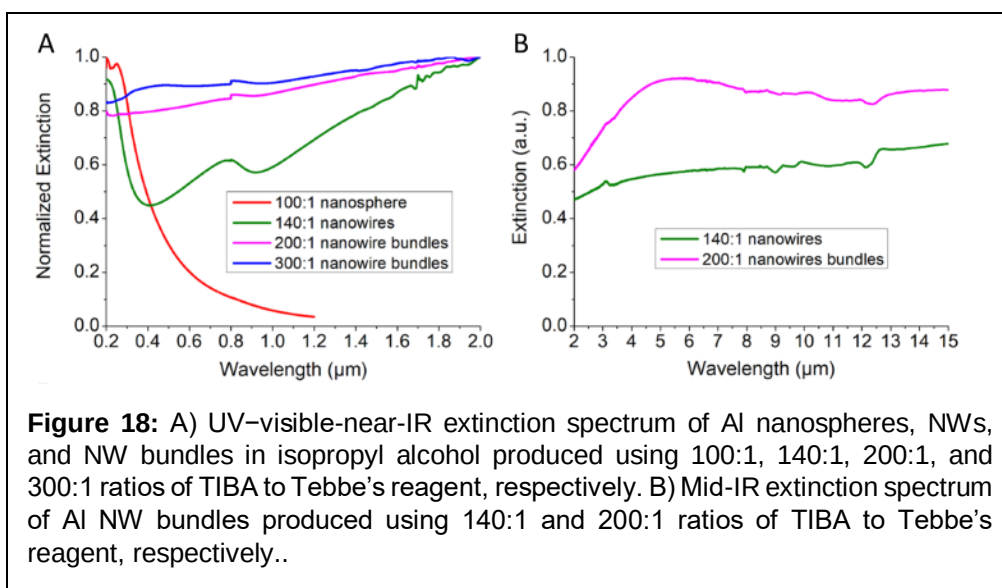
A family of branched nanowire Al nanocrystals can be synthesized when triisobutylaluminum (TIBA) is catalytically decomposed using Tebbe's reagent. The synthesis is sensitive to the precise

ration of Al:Ti, tunable from isotropic nanoparticles to branched nanowires to large clusters of interleaved wires. (Figure 17) The short axis of each shape is <50 nm, while the wires can be



several hundred nanometers to a few microns long. The wires are formed by growth in the <100> direction, the first demonstration of this growth direction in Al nanoparticles. This work demonstrates the wide potential for exploration of the field of catalyst-based shape control for Al synthesis, with the combination of two previously studied syntheses yielding completely novel particles.

The wide range of morphologies attainable with this synthesis means that a

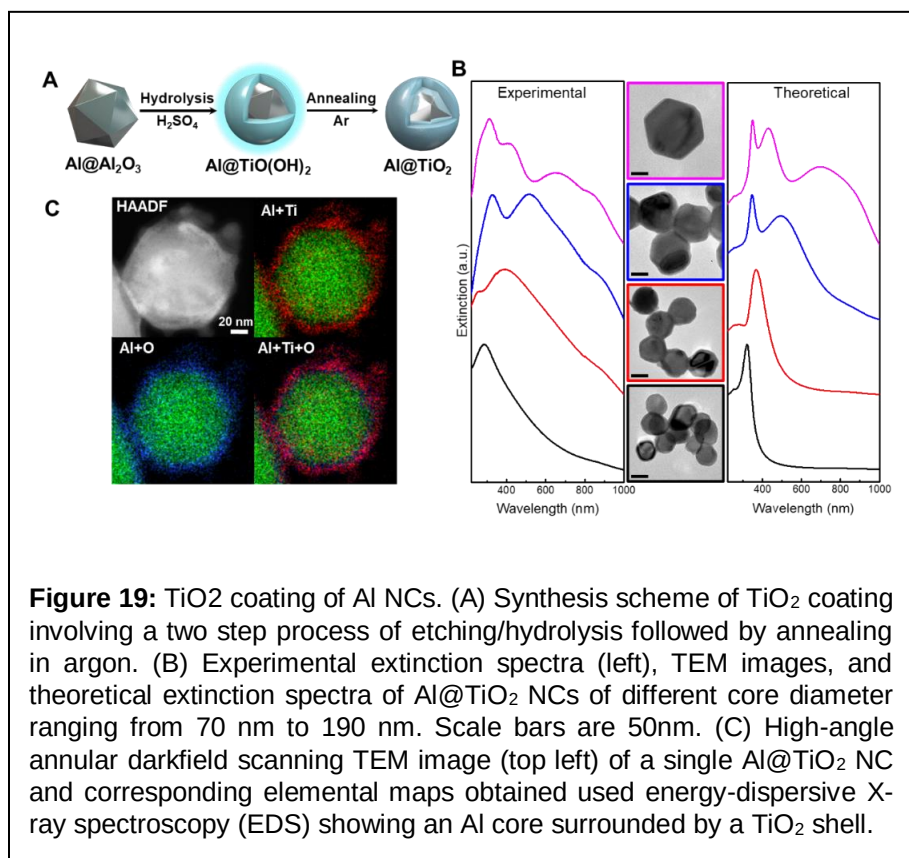


wide range of optical properties can be obtained as well. The small isotropic particles absorb strongly in the UV region, while the branched wires and clusters can be tuned across the visible and well into the IR region. IR spectra of the nanowires and bundles show broadband extinction at wavelengths as long as 15 microns. Additionally, calculations show that due to their narrow width, the Al nanowires strongly absorb in the infrared – this property is unique, as any other shape Al nanoparticle large enough to resonate in the infrared would be purely scattering. This strongly absorbing nature is potentially useful for a variety of applications, including localized heating from infrared sources and combustion studies.

Al@TiO₂ Core@Shell Nanoparticles

Titanium dioxide (TiO₂) surface coatings have been developed for Al NCs due to the well-studied photocatalytic properties of TiO₂, and as a protective layer to prevent oxidation of the Aluminum nanoparticle. The TiO₂ coating also makes the Aluminum nanoparticle water soluble, and removes the thin alumina coating on the aluminum nanocrystals. The functionalization proceeds in two steps. First, the native Al₂O₃ layer of the NCs is etched away in an acidic environment, increasing the local ionic strength and the local pH. These effects cause hydrolysis of dissolved TiOSO₄ and

deposition of TiO(OH)₂ only around the Al NC. Then, in a second step, the TiO(OH)₂ layer is annealed in argon at 450 °C for 1h, forming an anatase phase TiO₂ shell around the Al core (Figure 19 A). The TiO₂ coating procedure works well for particles of arbitrary size and shape, imparting new surface chemistry and reactivity to any of the Al nanoparticle syntheses developed. The optical characteristics of this core-shell geometry leverage the tunable plasmonic antenna effect of the Al core and the direct absorption of the TiO₂ shell for

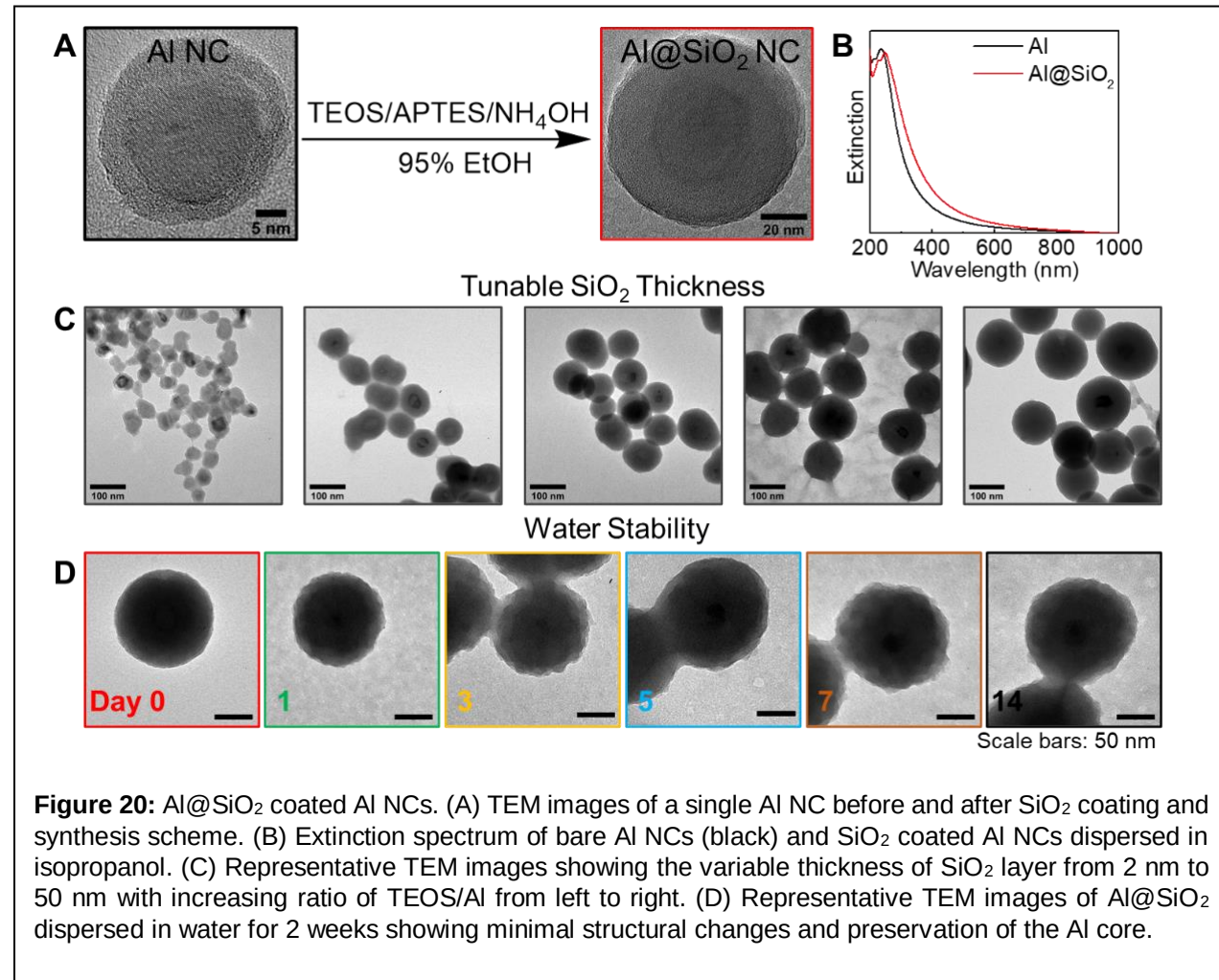


tailored optical and photochemical applications. TiO₂ alone is only able to absorb UV light below 400 nm, while the Al core can efficiently capture light at a designed energy, dictated by the core diameter (Figure 17B). The elemental composition of the Al@TiO₂ particles has been confirmed using High-angle annular dark field (HAADF) TEM imaging paired with elemental mapping via

energy dispersive X-ray spectroscopy (EDS) (Figure 17C). When the Al plasmon energy lies below the band edge of the TiO_2 shell, the Al core acts as an antenna for visible light, generating energetic hot carriers which can be transferred to the TiO_2 shell for inducing chemical transformations.

Al@SiO₂ Core@Shell Nanoparticles

Silicon dioxide (SiO_2) coatings have also been developed for Al NC functionalization to improve their stability in aqueous and humid environments. Al is readily attacked by moisture both in air and in solution, reducing their usable lifetime, degrading their nanoscale structure, and eliminating their optical properties. SiO_2 functionalization was accomplished by adapting the well-established Stöber method to form nanoscale SiO_2 coatings. Al NCs are suspended in 95% (v/v) ethanol/water with a small amount of ammonium hydroxide. Then tetraethyl orthosilicate (TEOS) and (3-aminopropyl)triethoxysilane (APTES) are added to form a conformal shell of amorphous SiO_2 around the particles (Figure 20 A). The amorphous SiO_2 layer minimally impacts the optical



properties of the particles, causing a slight red-shift due to local dielectric change (Figure 20B). The SiO_2 coating layer can be easily tuned from 2–45 nm by altering the ratio of TEOS/Al (Figure

20C). This procedure works extremely well for Al NCs as the silicate precursors readily bind the native Al_2O_3 layer on the particle surface. Additionally, the SiO_2 layer can be subsequently functionalized with molecules such as PEG or acids/bases to change their water solubility/surface charge, respectively. SiO_2 functionalization can be implemented on Al particles of arbitrary size and shape, allowing for dramatic water stability increases for even particles of very small size. To illustrate this stability, ultra-small Al NCs that efficiently absorb and scattering UV light (~ 240 nm) were coated with SiO_2 and dispersed in water. TEM imaging reveals minimal structural changes to the Al core over the course of two weeks in water (Figure 20D). Al@ SiO_2 NCs are currently being used for photothermal heating applications where water stability is a critical factor and may be useful in other applications where humidity and moisture are intrinsic to the system.

Structural Hole Burning through Selective Photothermal Reshaping of Au Nanorods

We developed a facile, generalizable approach toward constructing an optical transparency window by selectively reshaping Au nanorods through monochromatic laser irradiation. The two-step process begins with synthesizing and mixing nanorods of various sizes to produce a spectral plateau. We prepared a spectral plateau between 600-1100 nm by mixing Au nanorod batches of twelve different sizes. Then this solution is irradiated with a monochromatic laser such that nanorods with transverse localized surface plasmon resonances (LSPRs) on resonance with the laser will reshape while nanorods sufficiently off resonance will not. We irradiated the solution with an 800 nm resonant laser to generate an optical transparency window through selective photothermal reshaping. Interestingly, the window minima is not at the resonant laser wavelength, which we attribute to the partial reshaping of the nanorods and not by a full melting process. We investigated this effect through theoretical modeling and time studies in order to predict the position of the transparency window with respect to the resonant laser wavelength.

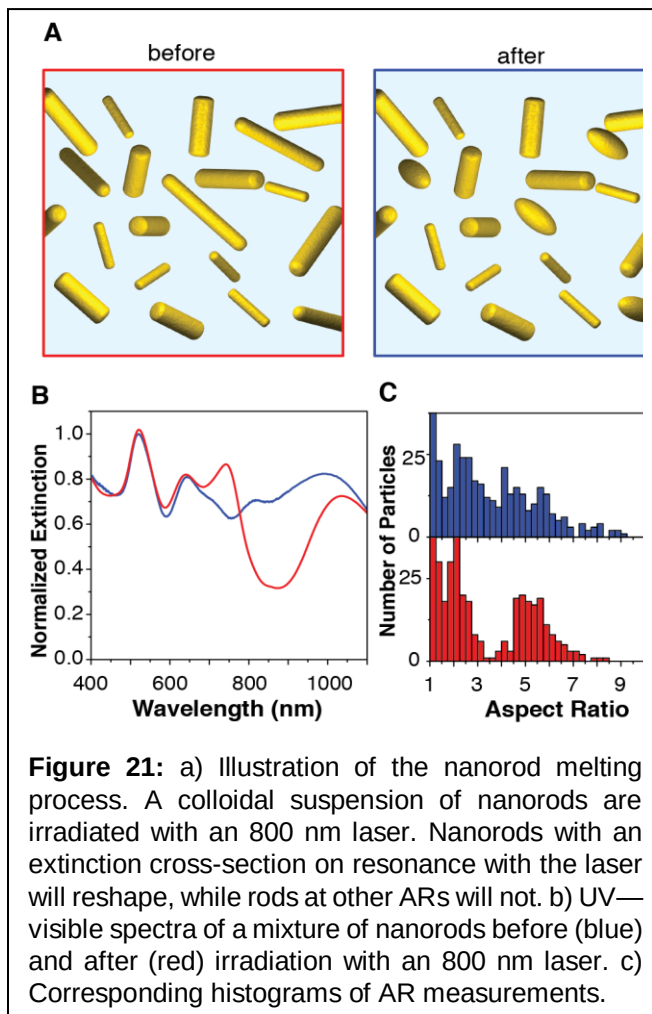


Figure 21: a) Illustration of the nanorod melting process. A colloidal suspension of nanorods are irradiated with an 800 nm laser. Nanorods with an extinction cross-section on resonance with the laser will reshape, while rods at other ARs will not. b) UV—visible spectra of a mixture of nanorods before (blue) and after (red) irradiation with an 800 nm laser. c) Corresponding histograms of AR measurements.

To achieve partial reshaping necessary for an optical transparency window, the average temperature of the nanorods during irradiation must be less than the melting temperature. The window dip minima position, depth, and width can be modified by altering the laser conditions as well as the time of irradiation, demonstrating the versatility of this process. We anticipate these results to build upon other means

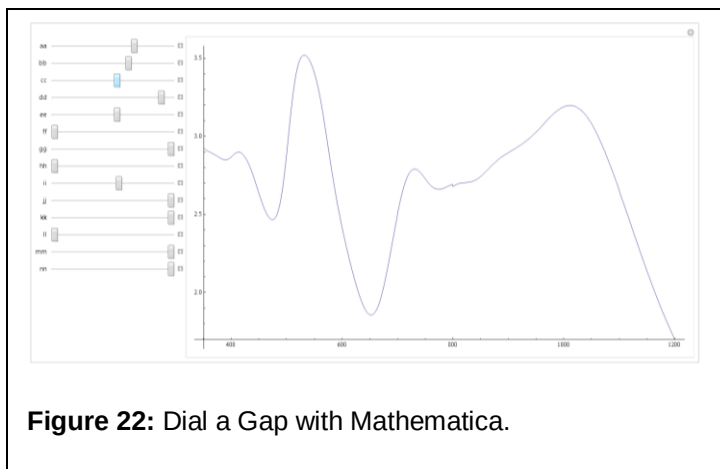


Figure 22: Dial a Gap with Mathematica.

of delivering an optical transparency window as well as guide principles toward photothermal reshaping of nanorods of various ARs. We developed a Mathematica program “Dial-a-gap” in which one can input the sizes of the available nanorods and move a set of sliders to modify the spectrum of the mixture of nanorods to get a transparency window in the desired wavelength range. (Desantis 2016)

Imaging Through Scattering Media

Imaging objects through plasmonic nanoparticle solutions depends upon more than just the extinction spectrum of the solution. It depends strongly on both the absorption and scattering properties of the constituent nanoparticles. In this project we are investigating and quantifying the image quality transmitted through a nanoparticle solution. We investigated the contributions from the nanoparticles scattering and absorption, the two main decay mechanisms on image quality. The transmitted images were quantified using analyses techniques originally developed for image processing.

In a simple demonstration of the technique we fabricated a mixture of two different sized nanorods. The normalized extinction spectrum of the mixture is in Figure 23a. The mixture has two peaks at 637 nm and at 877 nm with a window around 750 nm. We used a bright field Köhler illumination setup for imaging a target through nanoparticle solutions. We employed a white light fiber optic illumination source along with wavelength selective bandpass filters from 450-900 nm wavelengths with 50 nm interval. For imaging, we used a CCD camera sensitive in 400 nm – 1000 nm wavelength range. With this optical setup we imaged a US Air Force (USAF) resolution target conforming to MIL-STD-150A standard which is used to test the resolving power of optical imaging systems. We placed the aqueous nanoparticle solution in a quartz cuvette directly in front of the camera so that the nanoparticle solution only influences the image of the target and not the illumination light.

Human visual perception is highly adaptive for extracting structural information from a scene which we take into consideration in the quality metric called structural similarity index or SSIM. In addition to concentration, another way to tune the optical density through which we image is to control the optical path length through the nanoparticle solution. Fig 23a shows the normalized images of groups 4 to 7 of USAF resolution target obtained through the solution with optical path lengths of 10 mm, 5 mm, 2.5 mm (top three panels) and through water (bottom panel), as presented in Fig 23b. The SSIM of the obtained images through 2.5 mm optical path length is wide because the optical density is below threshold at various wavelengths. However, at the path length of 5 mm, only three out of ten wavelengths remain above threshold and the window becomes narrower. with 10 mm optical path length, only the minimum optical density point near 750 nm wavelength remains above the threshold and the window through the nanorod mixture solution becomes even narrower for the imaging system. This is a versatile technique to tune the image distortion properties of nanoparticles by using the same nanoparticle solution. Among various image quality measures, SSIM provides realistic information regarding how clear or distorted an image is when transmitted through plasmonic nanoparticles conforming to human visual system. This provides a design paradigm to investigate other nanoparticle solutions with a transparency window for transmitting images.(Tanzid 2016)

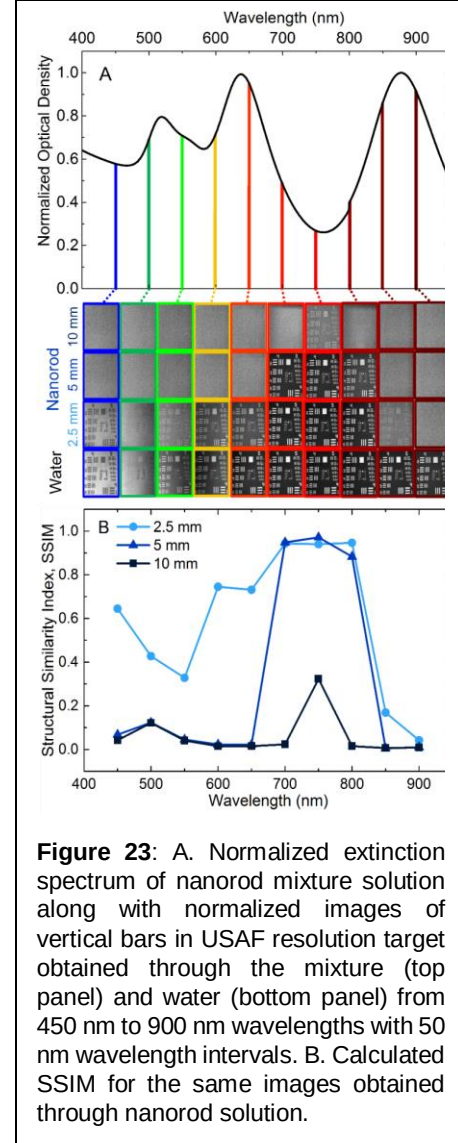


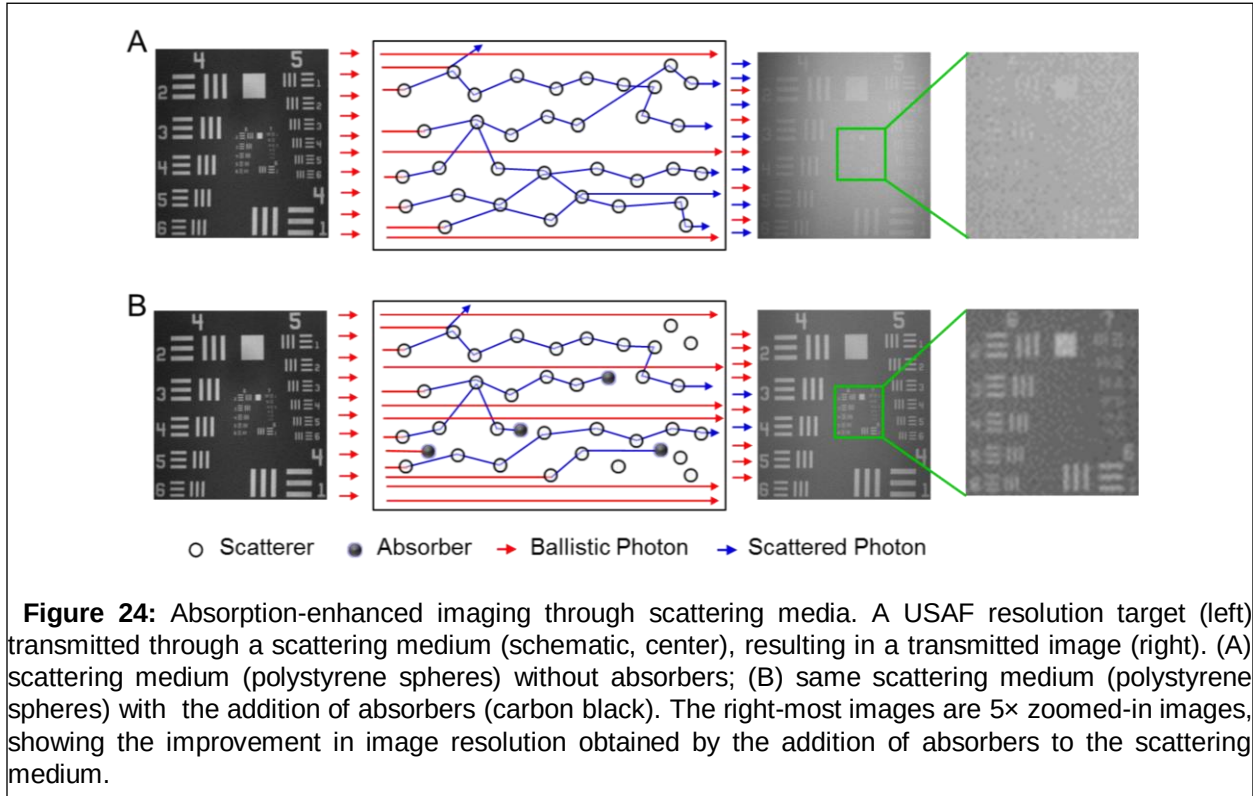
Figure 23: A. Normalized extinction spectrum of nanorod mixture solution along with normalized images of vertical bars in USAF resolution target obtained through the mixture (top panel) and water (bottom panel) from 450 nm to 900 nm wavelengths with 50 nm wavelength intervals. B. Calculated SSIM for the same images obtained through nanorod solution.

Absorption-Induced Image Resolution Enhancement in Scattering Media

Highly scattering media pose significant challenges for many optical imaging and communications applications due to the inherent loss of information caused by the scattering process. Absorption can also result in significant degradation of image quality even in diffuse systems where it is commonly ignored. In this work, we showed both experimentally and computationally that absorption can actually improve the quality of images transmitted through a scattering medium in certain regions of parameter space.

This absorption-induced image enhancement is illustrated schematically in Fig. 24. When an image is transmitted through a scattering medium, the transmitted image is degraded due to the scattering of photons into trajectories not associated with the original image (Fig. 24A). By introducing absorbers into the scattering medium, image quality can be improved, since the

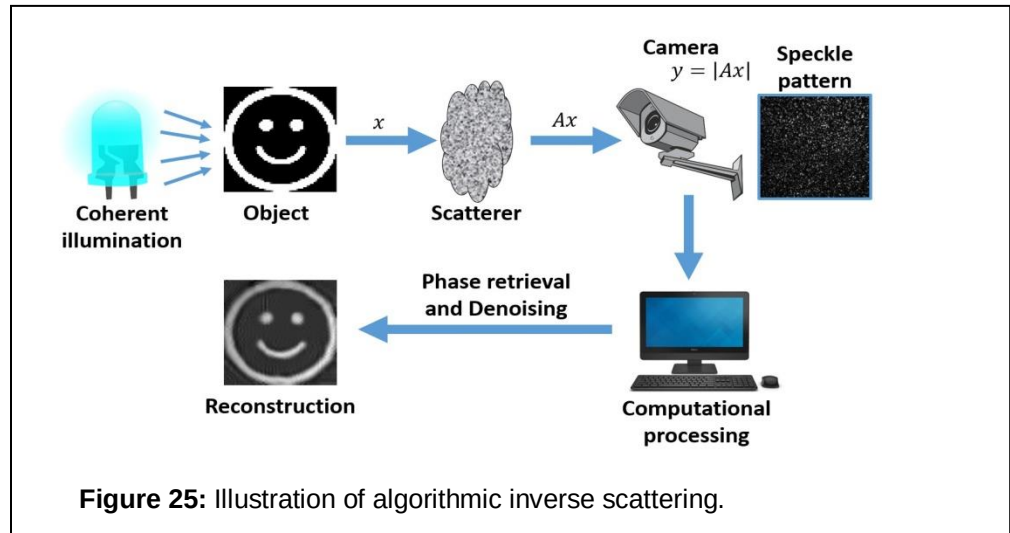
absorbers will selectively remove more scattered photons than ballistic photons (Fig. 24B). The 5× zoomed-in images show that higher resolution images are recovered with the addition of absorbers (carbon black) into the scattering medium (polystyrene).



However, this image enhancement varies significantly depending on the absorption and scattering coefficients and the anisotropy factor of the scattering medium. Using broadband absorbing and scattering nanoparticles, while keeping the anisotropy factor constant, we showed that a sufficiently high scattering coefficient is necessary for the improvement in image quality and resolution. Moreover, we found that the addition of absorbers to a forward-scattering medium (e.g. biological tissue) has a negligible effect on image quality as compared to an isotropic scattering medium. For analyzing the image quality and resolution quantitatively, we used structural similarity index (SSIM) and cut-off spatial frequency from modulation transfer function (MTF) of a resolution target, respectively. This work has consequences for applications in imaging through media that exhibits both scattering and absorption, such as biological tissue, as well as for engineering media for optimal imaging and image transmission, or communication. (Tanzid 2016).

Computational Imaging Through Scattering Media

Seeing through scattering media remains one of the most challenging problems in imaging system design at all scales, from the microscopic to macroscopic. At the microscopic level path lengths are short, but a great many interesting subjects



(e.g. biological tissue such as skin, brain and bone) are densely scattering with only miniscule scattering depths. In remote sensing, path lengths are several orders of magnitude greater than optical wavelengths so that even small amounts of scattering (e.g. from smog, smoke, dust) can accumulate to drastically reduce visibility. A number of techniques have been introduced independently in computer vision, computer graphics, microscopy, physics, optics, and remote sensing research communities to remove the effects of scattering and provide greater visibility over longer distances possible than using conventional photography. The principles by which existing techniques reduce the effects of scattering are independent and complimentary. While each of the existing techniques result in a slight improvement in imaging performance they can be combined to produce a compounding increase in performance since their principles of operation are complimentary. In this research project we performed a comprehensive mathematical analysis, theoretical modeling, computer simulation, and experimentation in a laboratory setting to understand the various parameters that affect imaging performance in the presence of scattering.

Our approach to the problem is

- to develop a mathematical framework, with associated models and algorithms for designing and characterizing imaging through scattering media and develop practical methods for improving imaging performance.
- develop a novel computational deblurring based techniques for improvement in imaging performance through scattering media.

A transmission matrix describes the input-output relationship of a complex wavefront as it passes through/reflects off a multiple-scattering medium, such as frosted glass or a painted wall. Knowing a medium's transmission matrix enables one to image through the medium, send signals through the medium, or even use the medium as a lens. The double phase retrieval method is a recently proposed technique to learn a medium's transmission matrix that avoids difficult-to-capture interferometric measurements. Unfortunately, to perform high resolution imaging, existing double

phase retrieval methods require (1) a large number of measurements and (2) an unreasonable amount of computation. In this work we focus on the latter of these two problems by developing a new phase retrieval algorithm that is significantly faster than existing methods. As a result, we achieve a $100\times$ reduction in computation times, thereby allowing us to image through scattering media at state-of-the-art resolutions. In addition to these advances, we also release the first publicly available transmission matrix dataset. This contribution will enable phase retrieval researchers to apply their algorithms to real data. Of particular interest to this community, our measurement vectors are naturally i.i.d. subgaussian, i.e., no coded diffraction pattern is required.

- We developed a coherent inverse scattering method that is based upon characterizing the effect of a scattering media as a transmission matrix and using computational phase retrieval methods to both efficiently acquire the transmission matrices and then later to perform imaging in scattering media.
- We characterized the performance of the algorithm and developed a novel efficient algorithm for inverse scattering.
- We captured a large dataset of transmission matrices for different scattering media and made these transmission matrices and the entire dataset publicly available. (Metzler 2017)

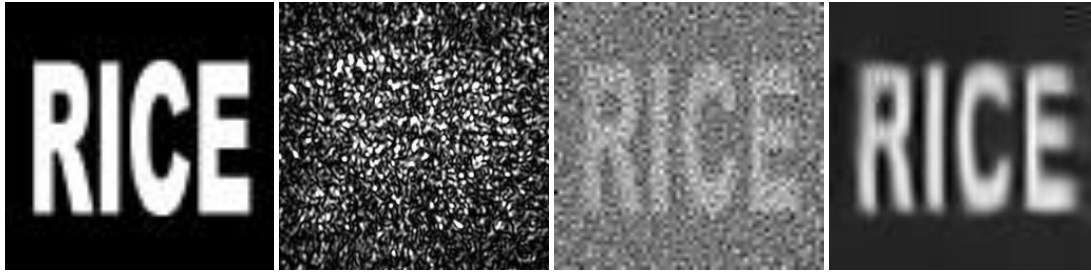


Figure 26: Example results of inverse scattering: (Left) ground truth image in the absence of scattering, (Middle-Left) Captured image in the presence of scattering, (Middle-Right) Reconstructed image using inverse scattering algorithm, (Right) Denoised reconstruction.

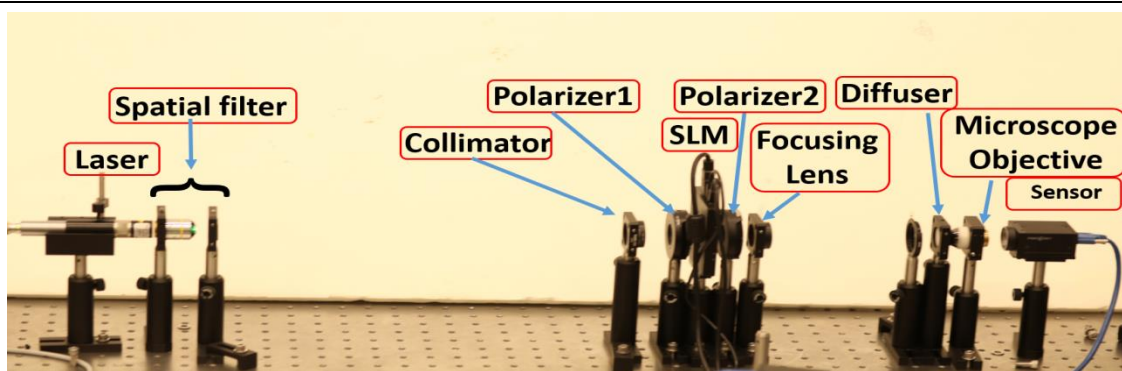


Figure 27: Photograph showing the experimental setup for imaging through scattering media.

In this project, we explored a linear systems characterization of scattering media and utilized this characterization for imaging through scattering media. The gold standard to image through very thick and stable scattering media is inverse scattering with optical transmission matrices (TMs). A TM characterizes the input-output relationship of a coherent light source as it passes through a multiple-scattering medium. The scattering process is linear and thus incident light $x \in \mathbb{C}^N$ will produce an output $z \in \mathbb{C}^M$, where $z = Ax + \varepsilon$, A is the TM, and ε represents noise. Imaging through scattering media with transmission matrices method assumes that you have access to the far side of the scattering media for calibration, which allows you to characterize the relation between the input field, on a spatial light modulator (SLM), and the output field, on a camera. When dealing with coherent light, the forward scattering process is linear in field and with the incoherent light the forward scattering process is linear in intensity and so the output field/intensity is related to the input field/intensity by a matrix A , which is known as the TM. If one first measures the TM, one can then “invert” the scattering process and image through or even inside the scattering medium, potentially using phase retrieval algorithms. However, learning a high-resolution TM is computationally challenging. We have developed a fast phase retrieval algorithm to learn a high-resolution TM in practical time. In this report, we discuss the mathematical models underlying transmission matrix methods and present our fast and robust to noise phase retrieval algorithm which is used to learn TMs under coherent (narrowband) and partially coherent (broadband) illuminations via various mathematical models.

In addition we have developed two analytical models for light scattering through scattering media: a narrowband (linear field) and broadband (linear intensity), to learn our TMs.

We have also developed algorithms for the inverse scattering using a phase retrieval technique. This method requires solving tens of thousands of phase retrieval problems. To accelerate this task, we have developed a fast and robust to noise algorithm which lets us learn a high-resolution TM in a few hours in comparison to million CPU hours required with previous methods.

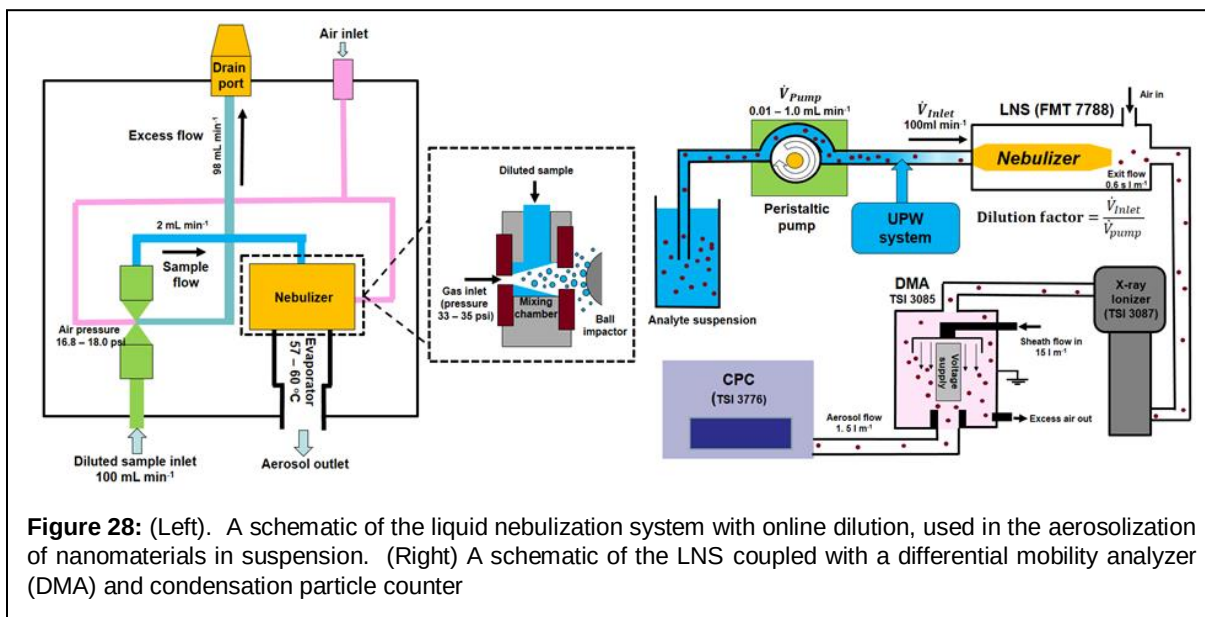
Aerosolization of Nanomaterials

Unique transmission windows in the visible and infrared range arise in nanomaterials of (1) unique chemical composition coupled with (2) unique morphology (e.g. core shell, fractal). It is hence necessary to develop techniques to characterize simultaneously the structure and chemical compositions of such nanomaterials. Further, for the use of these nanomaterials in a variety of applications, it is necessary to embed them within passive substrates in a manner which minimally disturbs their properties, and facilitates stable performance over long periods of time.

To introduce these materials into the gas phase while preventing nanomaterial aggregation, we developed electrosprays (electrohydrodynamic atomization), which produce near monodisperse droplets in the 10nm – 10 μ m size range, adjustable by controlling the volumetric flowrate of liquid through the electrospray, and the electrical conductivity of the suspension. Through precise control of the droplet size, we can ensure that only one nanoparticle at most is present in each droplet, such that the size distribution (and structures) of particles in the gas phase are identical to those in stable liquid suspension. Only a single electrospray is necessary to introduce a sufficient number concentration of particles into the gas phase for structural and chemical analysis, however, to imbed materials on substrates with a noticeable influence on substrate properties, we intend to

use a multijet electrospray system (which will also be used for high volume aerosolization). We developed techniques to monitor the size shape chemical composition and physicochemical properties of aerosolized nanoparticles.

A schematic of the LNS-IMS system is presented in Figure 28 of the subsequent section. In the LNS, a nanomaterial suspension is rapidly mixed with ultra-pure water (at a dilution ratio of 100 to 10,000, which is controllable) and directed through a nozzle, generating micrometer scale droplets. With proper dilution, each droplet contains at most one nanoparticle and a negligible amount of non-volatile residue. Upon evaporation of solvent (water), the nanoparticles are then released into the gas phase, with their size, shape, and chemical composition preserved exactly. Subsequently, ion mobility spectrometry (IMS using a differential mobility analyzer and condensation particle counter) is used to measure the size distribution function for particles. With IMS measurements, a size and chemistry dependent calibration curve to directly infer the original suspension number concentration. A characteristic size distribution (for a gold nanospheres and nanorod sample from Nanocomposix) and the number concentration calibration curve were



developed .

The code used in conjunction of differential mobility analyzer-aerosol particle mass analyzer measurements to infer the two-dimensional size distribution function of nanomaterials is freely downloadable via the “Educational Resources” section of Prof. Chris Hogan’s personal website (<https://chrishogansite.wordpress.com/educational-resources/>). No login or password is required to download the code, and it is complete with sample data and a README.txt file explaining its use.

DMA-APM measurements

Ion mobility spectrometry, a gas phase analog to electrophoresis, only provides information on the gas phase equivalent size (mobility diameter, i.e. the diameter of a sphere with an identical diffusion coefficient in air). For structured nanomaterials, multidimensional shape characterization needs to be carried out. For this purpose we have constructed a differential mobility analyzer-aerosol particle mass analyzer (DMA-APM) system, in which particles are first mobility size selected with the DMA, and second mass selected with the APM. The APM functions by flowing particles through a passage between two rotating cylindrical shells; this rotating creates a mass dependent centrifugal force on particles. The centrifugal force is balanced by a apply a potential difference between the inner and outer cylindrical shells, and only particles with a specific mass to charge ratio, for which the electrostatic and centrifugal forces balance with one another, will exit the APM. Results to date, using ammonium sulfate particles (an analog for particles in the atmosphere) and aggregated soot nanoparticles (an analog for engine emissions) are shown in Figure 29. Because the soot particles are highly aggregated, chain-like structures, they have much less mass than ammonium sulfate at the same mobility size.

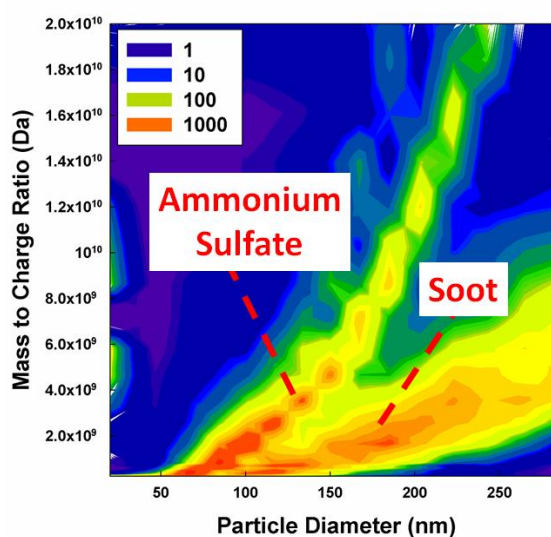


Figure 29: The two dimensional mass-size distribution (units of number per cubic centimeter) for a mixture of ammonium sulfate (a mimic for atmospheric particles) and soot from an acetylene-air flame (a mimic for engine emissions). Data were collected using a differential mobility analyzer, centrifugal aerosol particle mass analyzer, and a condensation particle counter, placed in series.

Because the soot particles are highly aggregated, chain-like structures, they have much less mass than ammonium sulfate at the same mobility size.

In summary, we have developed numerous techniques to modulate the line shape of the electromagnetic interaction of plasmonic nanoparticles with light. This was through the development of new bio compatible cost effective materials that can be deployed for large scale applications. We investigated and developed synthesis methods for a large variety of Aluminum nanoparticles that can be scaled up for real world applications. We developed and demonstrated the concept of a window – wall to engineer a transparency window and techniques to tune the position of the window achieved.

In addition we investigated the imaging of an object through scattering media and how the imaging maybe improved by the addition of absorbers. We demonstrated a 400% improvement in resolution using ZnO and polystyrene beads as scatterers and carbon black as absorber.

We developed techniques to aerosolize nanomaterials while maintaining their composition, size and shape and monitor the properties of the aerosol particles.