



ENI AWARD 2022

Energy Transition

Naomi Halas and Peter Nordlander

Winners

Antenna-Reactor Plasmonic Photocatalysis for Sustainable Hydrogen Generation and Delivery

Research Description

Halas

Naomi Halas is best known for showing how the nanoscale geometry of noble metal nanoparticles can control their optical properties. She was the first to introduce shape modification into the colloidal synthesis of coinage metal nanoparticles for the express purpose of controlling their optical resonance, which is due to their collective electron oscillations known as plasmons (**PRL 1997; CPL 1998**). Her work brought together two disparate fields; nanoparticle chemical synthesis and the physics of light-particle interactions. Her work has been a catalyst that merged these two distinct fields, giving rise to the field of Plasmonics. Her work has had an enormous impact on nanoscale optics, on nanoparticle synthetic chemistry, and has been precedent-setting in the design and development of nanoparticles for specific applications. In addition to her new synthesis approaches based on methods adopted from other fields such as surface science, her use of single nanoparticle microscopy rather than ensemble methods allowed for an unprecedentedly close comparison between theory and experiment (**Nano Lett 2004**). Her papers on nanoparticles of various geometries became citation classics largely because they encompassed both theory and experiment, and by collaboration with the theory group of Peter Nordlander she introduced a new level of experimental-theoretical synergy unheralded in the field of

nanoscience. She supplied the experimental demonstration and verification of Plasmon Hybridization Theory (**Science 2003**). Plasmon Hybridization is the electromagnetic analog of Molecular Orbital theory, and in this context, metallic nanoparticles of specifically controlled geometries can be conceptualized as artificial molecules. Based on the Plasmon Hybridization picture, she was able to create a very large variety of different types of metallodielectric nanoparticles, varying both shape and the number of metal and dielectric layers to control their plasmonic behavior and thus “tune” their optical properties (**ACR 2007, Chem Rev 2011**). Recently she has turned her attention to understanding the controlled synthesis of Aluminum nanocrystals, the most earth-abundant metal that supports plasmon resonances in nanoparticle form. Aluminum nanocrystals have a synthetic chemistry entirely unique to this element, depending on both the molecular structure of an organometallic catalyst and interactions with the solvent environment. Both catalyst and solvent stabilize the complex responsible for nucleating growth (**Nano Lett 2015; JACS 2019**) and can specifically direct Al nanocrystal growth into distinct morphologies, such as nanorods and nanocubes (**ACS Nano 2018; ACS Nano 2019**). She has also shown that Al nanocrystals can support surface-enhanced Raman spectroscopy (**Nano Lett 2017; ACS Nano 2019**), a property highly useful for low-cost sensing applications. Based on this fundamental work, Halas has pursued multiple innovative and practical applications for plasmonic nanoparticles. A prime example of this is her work with bioengineers and medical doctors, on photothermal cancer therapy. Together with bioengineer Jennifer West, they showed that Halas’s nanoshells, silica core-gold shell nanoparticles whose resonances are tuned to the near infrared spectral region of high physiological transparency, could be used for highly localized and controlled photothermal ablation of tumors when illuminated with a near infrared laser (**PNAS 2003**). This work stimulated great international interest in nanomedicine, and also generated great interest in the development of other near-infrared-absorbing nanoparticles for photoablation of tumors. Collaborating with a team of clinical oncologists, they showed that this same approach can be used to induce tumor remission in prostate cancer patients, eliminating the deleterious side effects associated with conventional prostate cancer treatments (**PNAS 2019**). Another area where Naomi Halas’s fundamental discoveries have stimulated societal impact is her discovery of “solar steam” (**ACS Nano 2013; PNAS 2013**), the localized heating of fluids by nanoparticles at liquid-air interfaces and its subsequent applications in water treatment. Working with civil and environmental engineers, this principle was utilized to transform membrane distillation, an energy-intensive distillation process under development for many years, into a solar-driven process called Nanophotonics-Enhanced Solar Membrane Distillation (**PNAS 2017**). Halas recently showed that by combining plasmonic nanoparticles, which act as optical antennas, with smaller clusters of catalyst nanoparticle “reactors” or even single atom reactive sites on their surfaces, provides a modular approach to photocatalysis that could potentially expand the way that chemical reactions are performed (**PNAS 2016; ACS Nano 2017**). Because illuminated nanoparticles undergo both photothermal heating and hot carrier generation, it is of central interest to distinguish thermal from hot electron-induced mechanisms in a plasmonic photocatalyst-driven chemical reaction. The antenna-reactor concept has also been shown to be useful for greatly reducing the reaction barrier towards ammonia decomposition (**Science 2018**), in a light-driven methane dry reforming reaction, resulting in a reaction temperature lower than the thermal process by more than 500 degrees (**Nat. Energy 2020**) and the light-induced cleaving of carbon-fluorine bonds (**Nat. Catalysis 2020**). These new types of nanoparticle-based photocatalysts are already under commercial development for real-world applications, which include low-cost Hydrogen fuel generation.

Nordlander

Peter Nordlander has made several pioneering theoretical contributions to the field of plasmonics. His theory of plasmon hybridization has laid the foundation for a rigorous yet intuitive understanding of how plasmons on adjacent nanostructures interact and hybridize to form collective modes. His prediction that Fano resonances can result from interactions between sub- and superradiant plasmon modes, has laid the foundation for the rational design of coherent plasmonic structures. His studies of quantum effects in plasmonic systems, establishing the limits of validity of classical electromagnetic descriptions and predicting new optical effects, have laid the foundation for the novel field of quantum plasmonics. His prediction of plasmon enhanced hot carrier generation has revolutionized the field of photocatalysis and paved the way for sustainable catalysis using renewable energy.

His development of the plasmon hybridization (PH) picture is the fundamental theoretical breakthrough that underlies the current conceptual view of plasmonic nanostructures as artificial molecules. In the PH method, originally published in **Science 302(2003)419**, he shows that the plasmons of complex metallic nanostructures can be expressed as linear combinations of plasmons associated with their elementary parts, analogous to how atomic orbitals interact and hybridize in molecular orbital theory. This concept is now a central paradigm in plasmonics research, used extensively by researchers across the physical sciences, engineering and biomedical technology.

In **ACS Nano 2(2008)707**, he predicts Fano resonances in plasmonic nanoparticle clusters and shows that such radiative coherence and interference phenomena result from the coupling of subradiant and superradiant collective plasmon modes of a common symmetry. This prediction has been experimentally verified in several papers including **Science 328(2010)1135**. In a study of nonconcentric ring-disk cavities (**Nano Lett. 8(2008)3983**), he showed that structural symmetry breaking provides a general mechanism for creating and tuning Fano resonances to specifically desired wavelengths, intensities, and lineshapes. He also predicted that plasmonic Fano resonances, due to their intrinsic nature as interference-based phenomena, would be highly sensitive to their local dielectric environment, providing localized surface plasmon resonance (**LSPR**) sensing capabilities far exceeding that of “standard” plasmonic structures. This important insight has established a new sensing paradigm, stimulating intense theoretical and experimental activity exploiting Fano resonances for chemical and biomolecular detection.

Nordlander has also pioneered the field of Quantum Plasmonics, studying plasmonic systems using fully quantum mechanical approaches. His studies on plasmon resonances in core-shell nanoparticles (**Nano Lett 3(2003)543**), fully verified their classically predicted tunability and yields optical spectra in excellent agreement with experimental results. In an application to a plasmonic dimer (**Nano Lett. 9(2009)887**), he showed that quantum effects such as nonlocal screening and electron tunnelling across gaps between adjacent nanoparticles can result in profoundly different optical properties and electric field enhancements than what is predicted by classical approaches.

Since 2011 Nordlander's work has focused on prediction and applications of hot carrier production from nonradiative plasmon decay (**Science 332(2011)702**). Such hot carrier generation in plasmonic nanoparticles can be exploited in a wide variety of plasmon-enhanced light harvesting applications such as photodetection and photocatalysis (**Nature Nano. 10(2015)25**). Direct hot carrier generation provide much better energy efficiencies for driving chemical reactions than conventional heating since only the electrons, and not the lattice, are heated. While the initial demonstrations were limited to reactions involving reactants that would adsorbed on plasmonic noble metal surfaces which are relatively inert, the introduction of the plasmonic Antenna-Reactor platform (**PNAS 113(2016)8916**), extended the applicability of plasmon enhanced photocatalysis to a full range of chemical reactions. The antenna-

reactor concept is based on the fact that the strong plasmonic near field around an antenna can induce excitations and hot carriers in a nearby reactor particle. The antenna can thus be chosen based on its ability to capture light of a desired wavelength and the reactor material can be chosen based on its ability to bind reactants. Using this approach Nordlander and co-workers have demonstrated highly efficient Nitrous Oxide decomposition (**ACS Nano 13(2019)8076**), defluorination of fluorocarbons (**Nature Catal. 3(2020)564**), Ammonia decomposition (**Science 362(2018)69**), and Methane Dry Reforming (**Nature Energy 5(2020)61**) and many other important reactions of societal relevance.