CHEMICAL REVIEWS

EDITORIAL

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Introduction to Plasmonics

The ability of noble metal nanostructures to manipulate light at the nanoscale has resulted in an emerging research area called plasmonics. This thematic issue of *Chemical Reviews* highlights recent progress in synthesis, assembly, characterization, and theory of conventional and unconventional metal nanostructures important in plasmonics, as well as the applications of these nanostructures in chemical and biological sensing, photothermal therapeutics, and solar energy. This issue is timely because although chemists and materials scientists have been at the forefront of leading current advances, a chemical perspective has not yet been compiled into a single special volume.

Our current understanding of plasmonics has been shaped by (1) an extraordinary array of **new methods for synthesizing nanostructures** including wet chemical methods, templated synthetic methods, and top-down lithographic methods. Metal particles can now be made with controlled size, shape, and arrangement, with heterogeneous composition that includes both plasmonic and nonplasmonic materials, and with a diverse and sometimes anisotropic functionalization that is chemically and physically compatible with the needs of medical technology, energy science, and electronic devices. (2) Important **advances in the characterization** of plasmonic structures. Beyond conventional optical and electron microscopy measurements, time-resolved studies of femtosecond and picosecond dynamics associated with the excitation of plasmons have revealed new features of electron dephasing and relaxation and plasmon-phonon interactions that determine plasmon-resonance quality and line shape, plasmon heating, and the interaction of plasmons with the nearby environment. (3) A **host of theory applications** that take advantage of the capabilities of computational electrodynamics software as well as concepts borrowed from antenna theory and from scattering theory. These advances in theory have made it possible for theory to lead in the development of structures that combine plasmonic excitation with diffraction effects, structures that optimize selective properties of plasmon resonances such as plasmon energy, width, absorption, and/or scattering for applications in refractive index sensing and surface enhanced Raman scattering (SERS), and structures with new applications in plasmon-induced heating, enhanced solar energy conversion, and coupling of plasmonics to chemical reactions.

This issue presents eight reviews that cover major themes in plasmonics, typically with an emphasis on the more chemical aspects. The review by Xia and co-workers describes the synthesis and assembly of silver nanoparticles and other plasmonic nanostructures using solution phase methods. A number of these methods have appeared in recent years which make it possible to synthesize particles with control of size and shape. In addition, the particles can sometimes be arranged on surfaces such that plasmon-mediated electromagnetic interactions between the particles lead to useful properties. Related studies of gold nanoparticles are also described as well as alternative preparations using top-down lithographic techniques.

The review by Cortie and McDonagh also focuses on nanoparticle synthesis but with an emphasis on hybrid and alloy nanostructures. A number of wet chemistry methods are examined, including deposition-precipitation, galvanic replacement reactions, coprecipitation, and templated growth. Such techniques make possible alloy and core−shell particles made from noble metals as well as hybrid materials involving plasmonic metals with Pt group metals, magnetic metals, alkalis, and groups 12 and 13 metals. Metallo-dielectric hybrids are also described, including combinations of plasmonic materials with II−VI semiconductors, oxides, and chalcogenides.

Mirkin and co-workers present a complementary approach to fabricate plasmonic structures using templated techniques for controlling the structure of nanoparticles. The review covers a broad array of structures, including hard and physical templates used to synthesize structured nanoparticles from solution, in porous templates, and by surface mask templates. Also, the use of soft templates is described, including biological templates and templates based on organic molecules, nanotubes, and polymers. Applications of the resulting nanostructures to SERS, localized surface plasmon (LSP) resonance sensing, photothermal therapy, and other effects are considered.

The review by Mayer and Hafner examines the use of plasmonic materials for refractive index sensing, which is one of the most important applications of LSPs. The sensitivity of the LSP wavelength to the structure of the nanoparticle plays a key role, and this paper also addresses issues with functionalization of the nanoparticles for different sensing applications (e.g., biological versus small molecule detection). Also highlighted here is the integration of nanoparticles with microfluidic platforms and optical fibers, and applications of this sensing modality to laboratory instruments and in vivo diagnostics.

The Hartland review discusses the dynamics of plasmon excitation in gold and silver nanoparticles, with an emphasis on information that can be obtained from femtosecond (fs) and picosecond (ps) time-resolved studies. The article also considers factors that influence plasmon line width as the nanoparticle size and shape are varied, including the intrinsic variation due to the bulk metal dielectric response, radiative damping effects, effects due to the environment surrounding the nanoparticle, and electron-surface scattering effects that broaden the plasmon in the small particle limit. A major portion of the paper focuses on the description of the breathing modes of nanoparticles, including their excitation due to electron−phonon interactions, and the variation of their properties with nanoparticle structure.

The review by Maier and co-workers provides a general description of the properties of plasmons and how electromagnetic theory and extensions thereof (such as plasmon hybridization) can be used to understand a number of interesting effects, such as dark plasmon modes and Fano resonances. The review also includes a description of nanoparticle arrays and other structures that can lead to unusual plasmon-photonic effects. Another discussion involves the use of plasmonic particles to control the local electromagnetic density of states, which enables the manipulation of light emitted by molecules near the particle surfaces. Applications of the plasmonic structures to

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surface enhanced fluorescence, SERS, plasmon-enhanced solar cells, and nanomedicine are included.

The underlying theory of plasmonic particles and other structures is presented in the review by Halas and co-workers. First, the traditional use of classical electrodynamics to describe the optical spectra of isolated silver and gold nanoparticles is presented, starting with Mie theory (analytical theory for spheres) and moving to numerical methods that can be used for any structure. Then, the bulk of the review is concerned with more modern topics that go beyond this traditional picture, including classical electrodynamics with nonlocal dielectric constants, theories that combine electrodynamics with quantum mechanics, and the use of a Fano description to model nanoparticle optical properties. Applications of these theory concepts to plasmon rulers, SERS, and surface enhanced infrared absorption round out the manuscript.

Another theory review by Jensen and co-workers focuses on the use of electronic structure theory to describe plasmonic properties. The bulk of the review describes how molecules interacting with metal particles influence infrared, fluorescence, and SERS spectra. First, few-atom clusters, which show molecule-like spectra, are discussed as well as monolayer-protected gold clusters. Then, a discussion of the quantum and classical comparison for larger nanoparticles where plasmonic behavior is more apparent is provided. Quantum mechanics coupled to classical electromagnetic theory circumvents the impossible task of describing particles with millions of atoms and has also made possible a description of both electromagnetic and chemical mechanisms for SERS. The review finishes with a discussion of chiroptical properties of metal particles with ligands, including circular dichroism and vibrational Raman optical activity spectra, and it also overviews nonlinear optical properties.

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Teri W. Odom is an associate professor of chemistry and materials science and engineering and Dow Chemical Company Research Professor at Northwestern University. Her research focuses on controlling materials at the 100-nanometer scale and investigating their size- and shape-dependent properties. She has developed massively parallel, multiscale nanopatterning tools that can generate a wide range of anisotropic, 3D plasmonic structures.

Odom has received numerous honors and awards, including a Radcliffe Institute for Advanced Study Fellowship at Harvard University, a Director's Pioneer Award from the National Institutes of Health, the Materials Research Society Outstanding Young Investigator Award, the National Fresenius Award from Phi Lambda Upsilon and the American Chemical Society, an Alfred P. Sloan Research Fellowship, a National Science Foundation CAREER Award, and a David and Lucile Packard Fellowship in Science and Engineering. Odom was the first Chair of the Noble Metal Nanoparticles Gordon Research Conference, whose inaugural meeting was in 2010. Also, Odom is an Associate Editor for *Chemical Science* and is on the Editorial Advisory Boards of *Chemical Physics Letters*, the *Journal of Physical Chemistry*, *ACS Nano*, and *Nano Letters*.

George C. Schatz is Charles E. and Emma H. Morrison Professor of Chemistry and of Chemical and Biological Engineering at Northwestern University. He received his undergraduate degree in chemistry at Clarkson University (1971), where he got to know two of the early people in the nanoparticle field, Milton Kerker and Egon Matijevic. He then completed a Ph. D. (1976) at Caltech, where he took courses in electrodynamics and scattering theory that cemented his interest in nanoparticle optical properties. He was a postdoc at MIT and has been at Northwestern since 1976.

Schatz has published three books and over 600 papers. Schatz is a member of the National Academy of Sciences (2005), the American Academy of Arts and Sciences (2002), the International Academy of Quantum Molecular Sciences (2001), and he has been Editor-in-Chief of the *Journal of Physical Chemistry* since 2005. Awards include Sloan and Dreyfus Fellowships, the Fresenius Award of Phi Lambda Upsilon, the Max Planck Research Award, the Bourke Medal of the Royal Society of Chemistry, the Ver Steeg Fellowship of Northwestern University, the Feynman Prize of the Foresight Institute, and the Debye Award of the ACS. He is a Fellow of the American Physical Society, the American Chemical Society, and of the American Association for the Advancement of Science. He was honored in the George C. Schatz Festschrift of the *Journal of Physical Chemistry A*, Vol. 113, 2009. He recently appeared on the Times Higher Education list of Top 100 Chemists of the Past Decade.