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Length Scales for Plasmon Modes in Metal Nanostructures and 2D Spectroscopy in the Ultraviolet

The collective motions of electrons in metal nanostructures and interfaces are known as surface plasmons, and they are the subject of intense interest in physical chemistry research.^{1,2} For nanoparticles, the surface plasmon modes are confined by geometry and produce resonances, whose frequencies depend on the size and shape of the particles.^{1,2} These localized surface plasmon resonances (LSPRs) give rise to enhanced absorption and scattering^{3,4} and are intimately related to the hot spots responsible for surface-enhanced Raman spectroscopy (SERS) in nanoparticle aggregates.^{5–7} In extended metal structures, the electron motions generate propagating surface plasmon polariton (SPP) modes,^{8,9} which are at the heart of a variety of biological molecule detection assays.

The Perspective by Odom and co-workers describes recent progress in understanding the frequency of LSPRs in metal nanostructures (Odom T. W.; You, E. A.; Sweeney, C. M. Multiscale Plasmonic Nanoparticles and the Inverse Problem. *J. Phys. Chem. Lett.* **2012**, 3, 2611–2616). They are specifically interested in complex shaped particles with multiple length scales, ranging from a few nanometers to a few micrometers. The spectra of these particles are extremely complicated. If the particle/aggregate shape and structure are known, then the spectrum can be calculated using numerical approaches, such as the discrete dipole approximation.^{10,11} However, the inverse problem of finding a structure that will produce a specific spectrum is more difficult. Odom and co-workers outline a library approach to this problem and also discuss the application of their multiscale metal nanostructures to SERS.¹²

The Perspective by Spoto and Minunni (Spoto, G.; Minunni, M. Surface Plasmon Resonance Imaging: What Next? *J. Phys. Chem. Lett.* **2012**, 3, 2682–2691) describes a different type of system, surface plasmon resonance imaging (SPRi) utilizing thin metal films.^{13,14} In SPRi devices propagating SPP modes are launched at the metal–dielectric interface using a prism or grating coupler. The SPP modes are sensitive to the properties of the dielectric¹³ and can be used for detection of biomolecules.¹⁵ The focus of the Perspective by Spoto and Minunni is on optimizing the surface chemistry of the metal dielectric interface to enhance sensitivity in SPRi devices (Spoto et al.). Applications of these devices include detection of markers for diseases and antidoping efforts in athletics.

Finally, the current issue of *The Journal of Physical Chemistry Letters* also contains a Perspective from the Moran group on two-dimensional (2D) coherent spectroscopy in the ultraviolet region (West, B. A.; Moran, A. M. Two-Dimensional Electronic Spectroscopy in the Ultraviolet Wavelength Range. *J. Phys. Chem. Lett.* **2012**, 3, 2575–2581). These types of experiments are well-known at infrared wavelengths and have been used to examine dynamics in a variety of different systems.^{16–19} The Perspective by Moran and co-workers discusses the challenges associated with performing ultrafast 2D experiments at ultraviolet wavelengths. The authors also highlight several important chemical problems that can be investigated with this technique, such as internal conversion and cooling in DNA^{20,21}

and ultrafast photochemical reactions like ring openings in cycloalkenes.²²

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Notes

Views expressed in this Editorial are those of the author and not necessarily the views of the ACS.

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