Virtual Issue on Plasmonics

Nanophotonics studies the interactions of nanostructures with light, where interesting effects occur for many different materials, sizes, and shapes. For example, quantum dots absorb and emit light with a wavelength that exhibits a strong nanometer-scale size dependence due to quantum confinement. Tiny apertures at the ends of coated optical fibers localize light to the nanometer scale and can be used for near-field microscopy. Complex dielectric structures steer light through tortuous paths at subwavelength scales. Our third virtual issue in *ACS Nano*[1] focuses on plasmonics—the manipulation of light by metallic nanostructures due to resonant oscillations of their free electrons. Plasmonics is a highly interdisciplinary field that has experienced a surge of progress over the past decade due to advances in many areas: synthesis of new nanoparticle geometries, fabrication of unique nanostructure shapes, microscopy and microspectroscopy of individual nanostructures, and theoretical analysis to elucidate the underlying plasmon resonances. Powerful molecular sensing applications are enabled by plasmonic structures due to their strongly enhanced optical near-fields and their sensitivity to the local optical environment. Plasmonic structures allow surface-enhanced Raman spectroscopy (SERS) to detect molecular vibrations down to the single molecule limit.[2] Refractive index sensing by plasmonic structures results in label-free assays that also reach that ultimate limit.[3,4] The heat generated by absorption in plasmon resonant nanoparticles is exploited in nanomedicine for photothermal therapies and drug delivery, while their optical properties have been used for imaging contrast. *ACS Nano* has published many excellent articles on these and other topics in this diverse field. In this virtual issue on plasmonics, we highlight very recent papers that provide insight into how the field might continue to grow and to evolve.

The fundamental plasmon resonances of single, spherical nanoparticles are well-known,[5] and other shapes can be predicted computationally with high accuracy.[6] Furthermore, the effect of plasmonic interactions between nearby nanoparticles has been investigated. Interactions have a significant impact on the resonant mode frequencies and near-field enhancements.[7] Recently, it has been demonstrated that a rich set of spectral behaviors emerges in nanoparticle dimers and oligomers with broken symmetry. Four articles in the virtual issue provide illustrations of broken symmetry systems: nanosphere heterodimers,[8] offset disk-in-ring structures,[9] defective nanoparticle heptamers,[10] and misaligned nanorods.[11] These structures reveal a range of phenomena, including unusual directionality of the light-scattering properties, tunable Fano resonances, the enlightenment of dark modes, and new modes that arise due to conductive overlap and charge transfer between adjacent individual nanoparticles. These properties create new capabilities for manipulating light at the nanometer scale and new opportunities for highly effective molecular sensing. Two papers in this issue specifically illustrate this point. In one, substrates with fabricated mixed dimers of rods and rings were designed to have plasmon resonances at both the SERS excitation and emission wavelengths to enhance the resulting spectroscopic signal.[12] In the other paper, a different advantage of manipulating plasmonic dimers is highlighted. Gold and silver dimers were embedded at controlled locations within an aluminum oxide nanowire to allow spatial encoding of a SERS signal along the wire, thus dramatically increasing the information density that can be stored in these SERS tags.[13] Perhaps breaking the symmetry of the dimers themselves could one day result in further increases. These papers on broken symmetry plasmonic structures point to the need for facile, large-scale synthesis of arbitrarily shaped nanostructures of gold and silver. A possible path toward this capability is illustrated by an article on the metallization of DNA origami that demonstrates the principle with synthesis of Y-shaped gold nanostructures.[14]

Since plasmonic excitations decay in part by converting their absorbed energy into heat, plasmonic nanoparticles may act as nanoscale photothermal transducers to manipulate their environment. This effect is of special interest in nanomedicine since plasmon

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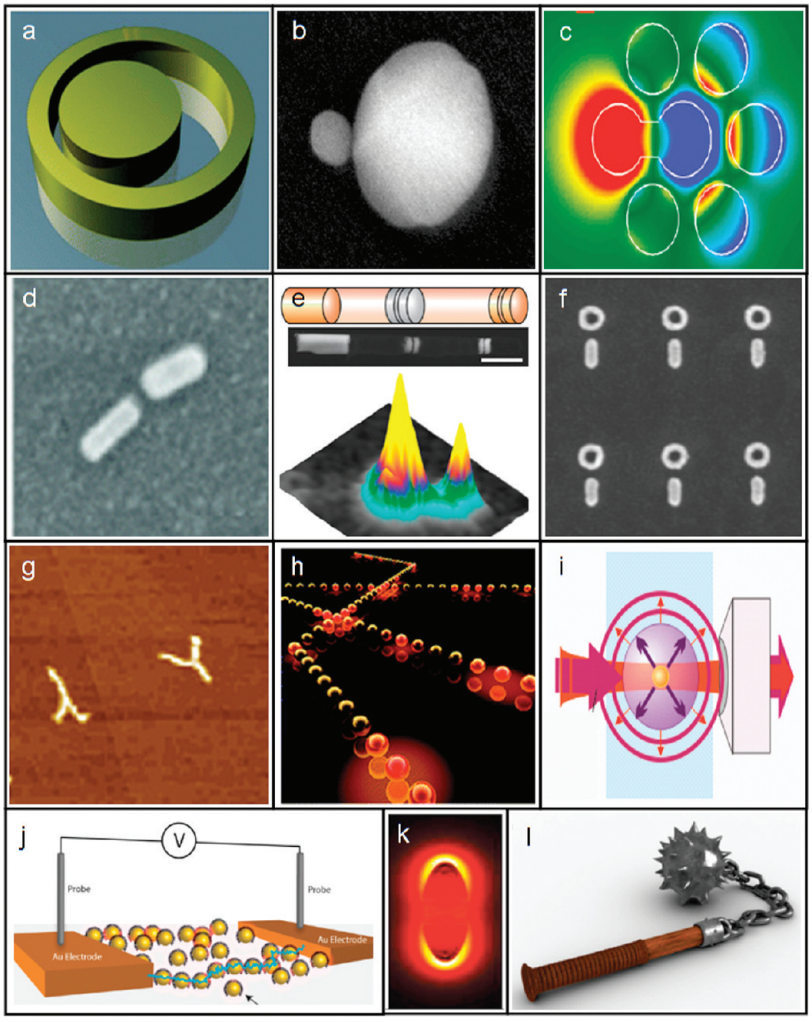

Figure 1. Representative figures from the articles featured in this virtual issue. Broken symmetries are presented by (a) an offset disk-in-ring structure,[9] (b) a nanosphere heterodimer,[8] (c) a plasmonic oligomer,[10] and (d) misaligned nanorods.[11] The two SERS applications are illustrated: (e) nanodisk dimers embedded in nanowires[13] and (f) mixed rod and ring dimers.[12] An AFM image of the metallized DNA origami is displayed in (g).[14] Nanoscale heat is illustrated in (h) calculations of temperature distributions in nanoparticle chains[18] and (i) plasmonic nanobubbles.[17] The interactions of plasmonics and molecular transport are illustrated in (j),[19] and the results of quantum calculations of plasmon resonances are displayed in (k).[20] Finally, a macroscopic model of an iron bearing nanostar is presented (l).[21]

resonances can be tuned to near-infrared frequencies where tissue absorbance is low. Plasmonic heating has been applied both in photothermal cancer therapies that directly destroy malignant cells and in drug delivery platforms.[15,16] Here, we feature two articles that describe novel aspects of nanometer-scale heating. The first concerns the excitation of plasmonic nanoparticles with high-power nanosecond laser pulses in a fluid environment.[17] Under these conditions, the rapid generation of heat forms a transient vapor bubble around the nanoparticle that grows to only hundreds of nanometers in diameter and lives only hundreds of nanoseconds before collapse. These plasmonic nanobubbles offer unique possibilities since they are transient, induce highly localized damage that is mechanical rather than thermal, and also possess large optical scattering cross sections. The exact mechanism of their formation and collapse is still under investigation. To understand such combined optical and thermal phenomena at the nanometer scale will require advances in theoretical and computational methods, such as those described in the second featured article on nanoscale heat.[18] Here, the authors have developed a combined electromagnetic and thermodynamic numerical method to study temperature distributions in and around plasmonic nanostructures under resonant illumination. Large non-uniform temperature

distributions were observed even at the nanometer scale, and it was found that they could be shaped and tuned by adjusting illumination angles and wavelengths. These articles suggest that there are rich nanoscale photothermal phenomena around plasmonic nanostructures that have yet to be explored.

Plasmon resonances are well described classically, usually by treating the nanoparticle metal as a continuum with a complex dielectric function, or by treating the metal's free electrons as an incompressible fluid. However, future areas of interest and applications will likely require a quantum mechanical description of plasmon resonances. For example, this virtual issue includes an article on the effects of plasmonic excitation of gold nanoparticle networks on electronic transport through conjugated molecules that link the nanoparticles.[19] Another article treats the plasmon resonances of gold nanorods with fully quantum mechanical time-dependent density functional theory and confirms the classical transverse and longitudinal plasmon resonances.[20] However, it was found that within 0.5 nm of the nanoparticle surface, a scale relevant to molecular transport and to SERS, the spatial distribution of the electrons must be considered.

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Of course, it is impossible to predict accurately which areas will flourish and carry plasmonics forward into the next decade, especially in such a diverse and creative field. As evidence, consider the final article in this special issue on magnetomotion of gold nanostars.[21] Nanostars exhibit polarized, multiwavelength, near-infrared scattering, so the authors grew nanostars around superparamagnetic iron oxide nanoparticles and used oscillating magnetic fields to cause the nanostars to spin. The spinning causes the scattering signal to blink at a known frequency, yielding a novel high-contrast imaging method for biological samples. We hope these articles and the creative research they describe convey the excitement in the field of plasmonics and demonstrate that there are still many challenges and fruitful areas to pursue.

Image courtesy of Faculty of Science, National University of Singapore

Prof. Andrew Wee of the National University of Singapore joins *ACS Nano* as associate editor.

In other journal-related news, we welcome frequent contributor Prof. Andrew Wee as our newest associate editor.[22−27] Prof. Wee is a professor of physics and is dean of the Faculty of Science at the National University of Singapore. He is well-known for his work on nanomaterials, including graphene, and molecular interactions with surfaces.

Finally, we have even more good news from Thompson Reuters—*ACS Nano* has now won its eighth ISI Rising Star, another record for any field.[28] Thank you for your continuing support of *ACS Nano*.

Jason H. Hafner
Associate Editor

Peter Nordlander
Associate Editor

Paul S. Weiss
Editor-in-Chief

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