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Shining a Light on the Molecular and Nanoscopic Worlds

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Light, the great unifier across science—from physics to chemistry to biology to medicine—is currently driving unprecedented, life-changing technologies. "Light" scientists and engineers have been recognized with recent Nobel Prizes for optical clocks and optical spectroscopy (2005, Physics, John Hall and Theodor Hänsch); optical fiber networks (2009, Physics, Charles Kao); efficient blue light emitting diodes (2014, Physics, Isamu Akasaki, Hiroshi Amano, and Shuji Nakamura); and super-resolution fluorescence microscopy (2014, Chemistry, Eric Betzig, Stefan Hell, and W. E. Moerner). The United Nations designated 2015 as the International Year of Light (IYL), and *ACS Photonics* is proud to be a sponsor for this celebration.

In this cross-journal virtual issue, we at *ACS Photonics*, *The Journal of Physical Chemistry A* and *B*, and *Analytical Chemistry* have compiled a diverse range of cutting-edge, light-based characterization and spectroscopy articles that showcase how light continues to be at the forefront of some of the most exciting developments by ACS authors. We will highlight advances from manipulating and squeezing light at the nanoscale to probing biological dynamics on time scales across 17 decades of time to developing new light sources for cold-molecule spectroscopy to designing imaging tools and optical sensors capable of ultrasensitive detection and to photodynamic therapy.

The first issue of *ACS Photonics* was published in January 2014. Within the past 18 months, there have been key advances in nanoscopic imaging, unconventional sensing, and materials-enhanced spectroscopy. Breakthroughs in nanoscopic imaging have included the demonstration of dark-field spectroscopy with single-molecule fluorescence sensitivity by clever means to suppress the background[1] and the use of laser-induced nanobubbles around gold nanoparticles to probe thermo- and plasma-mediated ultrafast cavitation regimes at the nanoscale.[2] Also, a combined low-temperature near-field spectroscopic imaging and transmission electron microscopy approach was able to resolve local defects and variations of crystal structure in single GaAs nanowires.[3] Also, in keeping with the hot topic of new imaging schemes, a far-field method based on composite photonic-plasmonic-structured illumination able to achieve super-resolution was proposed.[4]

Regarding unconventional sensing, new ways to measure thermal forces were realized using Janus particles (silica spheres with Au half-shells) trapped by optical tweezers, but also those controllably displaced via a laser beam were demonstrated.[5] Accessible devices such as smartphone cameras could resolve Raman signals with near-single-molecule blinking motion on plasmonic substrates,[6] while mid-infrared microspectroscopy based on quantum cascade lasers could generate narrow spectral lines similar to those in the visible range.[7]

With respect to materials-enhanced spectroscopy, confining both the laser beam and sample solution within a photonic crystal fiber enabled two-photon excitation to be supported over very long path lengths (>10 cm), which holds promise for ultrasensitive investigations of two-photon-induced processes in solution.[8] Functional materials have also been integrated and patterned onto optical fibers that could detect thin layers adsorbed in the near-fields of the fiber tip.[9] Also, as a prime example of materials enabling new photonics, graphene sandwiches enhanced a broad range of molecular absorption lines and not just those associated more narrowly with traditional plasmonic sensing substrates.[10]

The Journal of Physical Chemistry publishes significant advances in spectroscopy and dynamics. In *The Journal of Physical Chemistry A* papers, we have highlighted those that show how combinations of tunable light sources and clever experimental design can dramatically increase information from gas phase molecules. New light sources include free-electron lasers for wider ranges of tunable infrared and far-infrared radiation, such as the FELIX laser in The Netherlands,[11] high-resolution optical parametric oscillators,[12] vacuum ultraviolet sources such as advanced light sources with radiation in the 6–20 eV range corresponding to molecular ionization thresholds,[13] and chirped-pulse microwave sources for Fourier

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transform spectroscopy at ultrahigh resolution.[14] When combined with cryogenic isolation, the photodissociation dynamics of ultracold ions "tagged" with hydrogen or helium[11] and the detailed interaction potentials and reactions of atmospherically relevant neutral radicals and clusters become visualizable.[12] Further, isomer-specific spectra can be obtained for ions by combining ion mobility for "shape selection" with photodissociation or fluorescence spectroscopy methods.[15] Ultra-high-resolution rotational spectroscopy can also resolve specific rotational transitions for molecules with many conformers.[14]

In *The Journal of Physical Chemistry B*, we have selected papers that show how light is playing an essential role in probing structures and dynamics in biology. In particular, advances in applications of laser technology have directly revealed the underlying molecular couplings that give rise to biological function and hold promise for drastically improving fundamental understandings of biochemical interactions. For example, ultrashort (<8 fs) pulses consisting of only a few optical cycles can be used to elucidate the initial internal chromophore dynamics leading to biological activity.[16] Advances in 2D infrared spectroscopy to probe hydrogen–deuterium exchange on individual protein residues can provide a sensitive probe of interactions among molecules.[17] Occurring over longer times, protein–protein interactions occur on the microsecond to minute time scales, yet only the very strongest (and slowest) interactions are easily probed, with analytical techniques being highly model dependent. A quantitative application of fluorescence recovery after photobleaching (FRAP) addressed this problem to recover binding kinetics within live cells.[18] Similarly, fluorescence fluctuation-based correlation spectroscopy (FCS) was used to study highly concentrated samples by removing laser and environmental noise sources.[19] These studies enable a wider array of protein interactions in living systems to be studied and are complemented by the use of interferometric detection of backscattered light from individual nanoparticles to study membrane dynamics at very high frame rates.[20] Such uses of light and its interaction with biomolecules and nanoparticles offer unique ways to probe important biophysical interactions in both model and living systems.

In *Analytical Chemistry*, we have highlighted papers that advance the resolution of imaging techniques and sensor design architectures that demonstrate improved sensitivity and selectivity for molecular sensing. First, absorption spectroscopy from the visible through mid-IR wavelengths was achieved with a spatial resolution down to 20 nm using photothermal induced resonance (PTIR).[21,22] Fluorescence-enabled electrochemical microscopy (FEEM) was also able to image the transient concentration profiles of redox species generated on ultramicroelectrodes.[23] Far-field super-resolution optical imaging techniques could resolve fluorescence modulations at the single-molecule level within electromagnetic hot spots of metal nanostructures,[24] and nanoparticles with Gd complexes could be used as probes for near-infrared luminescence *in vivo* imaging by eliminating background noise.[25]

Second, light-based detection methods have shown improved sensitivity based on advances in sensor design. Localized surface plasmon resonance (LSPR) imaging of arrays of nanoparticles achieved high-throughput, label-free analysis of a wide range of molecular binding interactions across a large field of view (>1 cm^2).[26] Fluorescence anisotropy was also used to develop a homogeneous binding assay in an automated microfluidic chip to detect protein–ligand interactions.[27] A portable chip-based device was constructed to detect cocaine in human saliva by combining a microfluidic-based multiphase liquid–liquid extraction method with waveguide infrared IR spectroscopy.[28] In addition, sensors based on classical photonic structures such as soft 2D photonic crystal hydrogels and silicon microring resonators have been engineered to detect charged analytes.[29] Importantly, these sensors operate over a large dynamic range and a wide spectrum of refractive indices.[30]

We hope you enjoy this selection of papers (http://pubs.acs.org/page/vi/probing_fundamentals_light-matter_interactions) from our four journals that showcase how ACS authors are pushing light-based science and technologies and, dare we say, how they are helping lay the foundation for future Nobel quality science and recognition!

AUTHOR INFORMATION

Notes

Views expressed in this editorial are those of the authors and not necessarily the views of the ACS.

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