Photothermal and non-fluorescent imaging in microscopy and spectroscopy

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Special Issue Preface

Photothermal and Non-Fluorescent Imaging in Microscopy and Spectroscopy

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Photothermal microscopy harnesses the natural non-radiative heat release in the environment of an optical absorber upon irradiation. The associated field of thermo-plasmonics,[1] where absorption is enhanced by plasmonic effects in conducting objects, has spawned numerous applications in biology, materials science, and chemistry, including photothermal therapy, photoacoustic imaging, photothermal manipulation of nanoparticles, hot Brownian motion, creation and utilization of nano/micro-bubbles, and thermal- and hot-electron-induced photo(electro)chemistry. When a plasmonic nanoparticle is excited with light, the absorption of photons generates a cascade of interactions between electrons and phonons on a broad range of times extending from hundreds of femtoseconds to microseconds and beyond.[2] For example, electron−electron scattering takes place within hundreds of femtoseconds, whereas electron−phonon scattering happens on a time scale of picoseconds. Phonon−phonon interactions and diffusion lead to thermalization on hundreds of picoseconds to microseconds, depending on material and length scales. Transient pump−probe spectroscopy is often used to study the initial ultrafast electron−phonon dynamics, whereas photothermal heating of the environment, being slower, is better suited to photothermal imaging, the creation and control of nano or microbubbles, the generation of hot Brownian motion, and the photothermal manipulation of small objects. Photothermal microscopy[3] utilizes photothermally induced refractive index changes in the local environment of single nanoobjects down to a few nanometers in size, with recent applications in chiral plasmonic and magnetic nanostructures.[4] The method has recently expanded to the mid-IR range, opening a whole new field of chemical imaging by vibrational absorption.[5] In parallel to photothermal microscopy, another interference-based microscopy method, interferometric scattering (iSCAT) microscopy, has progressed spectacularly in the last several years and proven to be very complementary to the more traditional fluorescence-based microscopy methods.[6] In contrast to the frequency-filtering of photothermal microscopy by a lock-in amplifier, iSCAT microscopy uses spatial filtering to obtain background-free signals. This special issue covers several of the above-mentioned topics.

Traditional ensemble-based pump−probe spectroscopy uses low frequency (∼ kHz) lasers for ultrafast transient spectroscopy. However, sensitive single-particle detection benefits from higher pump and detection rates, which requires higher repetition rates (∼ MHz), potentially associated with a lock-in amplifier. The use of photodiodes as detectors limits measurement of a single particle's transient spectrum to point-by-point acquisition. Adhikari et al. (10.1021/acs.jpcc.4c01814) report an innovative time-resolved pump−probe setup including an on-chip lock-in detection that enables multiplex spectral detection of both electron dynamics and acoustic vibrations of single nanoparticles. Their proposed lock-in camera-based approach yields the time-resolved transient spectrum of a single gold nanodisk in a single measurement and thus enables probing electron−phonon dynamics at multiple wavelengths simultaneously. Willson et al. (10.1021/acs.jpcc.4c02984) apply the same lock-in camera-based method to wide-field transient absorption microscopy with high sensitivity and detect spatially varying photoexcited dynamics in a heterogeneous organic crystal. Mermoul et al. (10.1021/acs.jpcc.3c06400), in their perspective, review the field of ultrafast pump−probe spectroscopy of 2D materials and films that are a few atomic layers thick for optical probing with high spatial and temporal resolution and high sensitivity.

The heat released by an absorbing nanoobject into its surroundings spreads and creates a temperature gradient and thereby a refractive-index profile known as a thermal lens. Understanding this optical profile and the thermal relaxation in the environment is important for photothermal-based applications, particularly in biological systems. Typically, in a homogeneous medium, the temperature relaxation is often modeled by Newton's law of cooling. This is basically a simple differential equation that leads to an exponential decay with a single time constant; however, in an extended medium, heat diffusion leads to a much slower, nonexponential relaxation. Samolis et al. (10.1021/acs.jpcc.3c07022) report that exponential decay depends on external parameters such as the laser pulse width, the sample cell design, and the spatial resolution. They show that Newton's law of cooling does not

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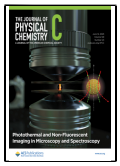

describe experiments in a satisfactory manner. In particular for cells and tissue, one needs to consider interfacial thermal conductance. Photothermal-induced temperature changes cause thermal expansion of materials. Anindo et al. (10.1021/acs.jpcc.4c08305) report photoinduced force microscopy providing high spatial and spectral resolution by measuring the van der Waals force between an AFM tip and the sample, demonstrating thermal expansion of the materials under mid-IR light absorption. By considering the local temperature change due to optical absorption of polarized light and its influence on the resulting force, they model their force measurements with a simple 2D framework incorporating variations in chemical composition. Rayaluru et al. (10.1021/acs.jpcc.4c04873) report an innovative photothermal IR spectroscopy method where the IR beam acts as the heating source and the probe beam is detected by total internal reflection. The method is based on the polarization change of the probe beam by the photothermal-induced change of refractive index and the ensuing deflection of the probe beam. Similar to a previous study in near-critical xenon, Wang et al. (10.1021/acs.jpcc.2c08575) report that the photothermal signal can be enhanced a thousand times in near-critical carbon dioxide which is much cheaper than xenon. In their perspective, West et al. (10.1021/acs.jpcc.3c04361) review the field of photothermal absorption spectroscopy and microscopy using nanomechanical resonators whose resonance frequency shifts upon photothermal heating. The sensitivity of nanomechanical resonators is high enough to detect single molecules and to record molecular spectroscopic fingerprints toward applications in surface science and medicine. In addition to photothermal microscopy, iSCAT microscopy harnesses interference between the scattered light and a reference. It has enormous potential for application in biological cells and tissues because of its sensitivity and its label-free character. However, iSCAT requires careful suppression of the spatially varying background signal that may present difficulties in the case of coherent laser sources. Wu et al. (10.1021/acs.jpcc.4c07989) present a low-coherence iSCAT microscopy method based on a light source with low spatial and temporal coherence to suppress speckle and nonspecific background signals. Thus, they detect gold nanoparticles with high sensitivity down to diameters of 10 nm, a highly promising result for label-free cell imaging. In a perspective paper, Carpenter et al. (10.1021/acs.jpcc.4c05878) discuss their recently developed interferometric scattering anti-Brownian electrokinetic (ISABEL) trap based on the combination of their previous ABEL trap with interferometric scattering for label-free detection and present applications in materials science, biology, and chemistry. A very promising and expanding fluorescence-free technique is stimulated Raman scattering (SRS) microscopy. Gao et al. (10.1021/acs.jpcc.5c00655) summarize a body of theoretical work on SRS microscopy and present a clear overview of fundamental concepts and pitfalls of this field.

An intriguing application of photothermal heating is the optical creation and sustainment of nano- or microbubbles around an absorbing nanoobject, for example, a metallic nanoparticle. Temperature gradients at the bubble's surface generate strong Marangoni flows. Dara et al. (10.1021/acs.jpcc.3c02263) report the control of the direction of such bubble-induced flows by asymmetric heating of nanoantenna arrays. Fluid flow extends tens of microns away from the heated area, and microparticle motion can be reversed by manipulating the focus position or the polarization of the heating light. In a later report, the same group (10.1021/acs.jpcc.4c08101) demonstrates a similar flow control with silicon nanodisk arrays instead of gold nanodisks and correlates the flow with bubble size. Silicon nanodisks are a more photostable alternative to gold nanoparticles and sustain higher heating powers. Kato et al. (10.1021/acs.jpcc.4c03779) report stable vapor-rich microbubbles upon local heating of a thin $FeSi_2$ film in a mixture of water and ethanol. In the concentration range of 1.5 to 50% ethanol content, the solutal-Marangoni force dominates the thermal-Marangoni force, and air-rich bubbles move toward higher-temperature regions. The Brownian motion of a heated nanoparticle in a liquid takes place in a gradient of viscosity produced by heat diffusion around the heating structures. Such Brownian motion of a heated nanoparticle has been dubbed "Hot Brownian Motion" (HBM) and was theoretically explored by Rings et al.[7] Guerra et al. (10.1021/acs.jpcc.4c07993) report direct experimental evidence of the "Hot Brownian" motion (HBM) by carefully measuring the translational and rotational motions and their difference across different particle sizes and pump laser intensities. They demonstrate that the experimental data are well captured by the HBM theory without need of any adjustable parameter.

Photothermal microscopy has been extensively used in biomedical science. Nakata et al. (10.1021/acs.jpcb.4c05785) report a photothermal study of malignant melanoma. Using gray-level co-occurrence matrix (GLCM) analysis, they characterize the degenerative and metastatic process and thus enable the detection of these processes. In another report, Watase et al. (10.1021/acs.jpcc.4c07036) photoexcite cytochrome C552 in a heme protein that releases heat into the surrounding water medium, shifting the O−H stretching frequency of water. Such experiments produce local temperature gradients and can modulate the thermal response of proteins, a promising avenue for the manipulation of live cells. Swain et al. (10.1021/acs.jpcc.4c00598) develop an innovative printing method for microscale-sized thermistors by using photothermally induced microbubbles. The temperature gradient in the microbubble generates a concentration gradient of metal ions that enables submicrometer resolution printing for biosensing. Shukla et al. (10.1021/acs.jpcc.4c07912) report optothermal trapping of metal nanoparticles in surfactant solutions and observe unexpected radial confinement and synchronized rotational diffusion of particles that are micrometers apart from the anchored nanoparticle, suggesting a new additional force responsible for thermophoresis.

Taken together, the contributions to this special issue paint a surprisingly wide landscape of new ideas and unexpected observations. The complexity and variety of phenomena triggered at micro- to nanoscales by photothermal heating raise many questions that will have to be answered in coming years. While experimental methods are still progressing, some contributions already demonstrate the first steps taken toward applications as diverse as the construction of new materials or the detection of rare entities, which is of high importance in biological and medical sciences. The examples given of images and manipulation of small objects hold great promise for applications, for example micropumps in microfluidics or sensitive assays for biomedical samples. This special issue proves that the exploration of this fascinating domain bridging physics, chemistry, and biology has just started.

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Notes

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