Widefield Infrared Photothermal Imaging and Spectroscopy

Kirill Kniazev [a], Evgenii Zaitsev[a], Loc Ngo [a], Zhuoming Zhang [a], Masaru Kuno [a,b*]

[a] University of Notre Dame, Department of Chemistry and Biochemistry, Notre Dame, IN, 46556, USA; [b] University of Notre Dame, Department of Physics and Astronomy, Notre Dame, IN, 46556, USA

ABSTRACT

Infrared photothermal heterodyne imaging (IR-PHI) is an ultrasensitive technique capable of achieving super-resolution chemical and morphological characterization of specimens via absorption of mid-infrared light. While early iterations of IR-PHI have involved point-by-point raster-scanning, here, we introduce a widefield modality to IR-PHI that utilizes ns-timescale infrared pump pulses synchronized to an ultrafast complementary metal-oxide-semiconductor camera to parallelize data acquisition. A 300-fold decrease in image acquisition time is realized, falling from 20 minutes to 4 seconds.

1.INTRODUCTION

Infrared absorption spectroscopy represents a facile tool for identifying chemical species using vibrational transitions in the mid-infrared (MIR) "fingerprint" region of the spectrum. In traditional infrared spectroscopy, spatial resolution is dictated by the Abbe diffraction limit, i.e. $\lambda/(2NA)$, where λ is the MIR wavelength and NA is the numerical aperture of the employed objective. Traditional IR microscopy measurements consequently possess a spatial resolution on the order of 5 μm given MIR wavelengths between 2.5–10 μm. Specimens in spectrally crowded environments, however, necessitate the development of super-resolution, MIR imaging and spectroscopic approaches.

To this end, tremendous advances have been realized recently to demonstrate MIR chemical imaging on the nanometer scale. Transmission electron microscopy-based electron energy loss spectroscopy is one such advance that yields images with sub-nm spatial resolution.[1] Tip-enhanced near-field optical microscopy[2] and atomic force microscope-infrared spectroscopy[3] are alternative approaches with sub-100 nm spatial resolution. In all cases, these techniques are costly, exhibit restricted fields of view, and are experimentally complex. A need therefore exists for a low cost, tabletop, super-resolution MIR microscopy/spectroscopy.

Infrared Photothermal Heterodyne Imaging[4] is an all optical, tabletop MIR microscopy and spectroscopy, possessing a ~300 nm spatial resolution. It employs a visible wavelength probe laser and a high NA refractive objective, in conjunction with a MIR pump laser, to achieve super-resolution MIR imaging and spectroscopy. IR-PHI operates via MIR-initiated photothermal changes in specimens wherein periodic heating leads to both local and transient changes in a specimen's refractive index and scattering cross section. Subsequent sample illumination with a continuous wave (visible) probe laser results in intensity modulation that can be detected using lock-in amplification. Extracted probe intensity modulation depths reflect the extent of MIR absorption by specimens. More details about the origin of IR-PHI contrast can be found in Reference[5]. By tuning the wavenumber of the infrared pump, local infrared absorption spectroscopy is possible.

IR-PHI has been implemented in a wide range of applications since its advent in 2016.[6] It has successfully imaged biological and soft matter specimens, including cells[6] and viruses.[7] For environmental science, IR-PHI has identified micro- and nano-plastics in complex environmental matrices.[8, 9, 10]. In soft condensed matter physics, the technique has been used to measure local stoichiometric variations in semiconductor thin films and bias-induced ion migration in lead-based perovskites.[11]

2. WIDEFIELD IR-PHI INSTRUMENTATION

Early iterations of IR-PHI involve collecting data in a point-by-point raster-scanning fashion. This entails using a closed-loop piezo stage to move specimens under the mutual foci of pump and probe lasers. More recently, a widefield modality has been incorporated into IR-PHI measurements.[12, 13] In the present study, we continue this push towards data parallelization by introducing an ultrafast, widefield modality to IR-PHI, called wIR-PHI, that features high temporal and spatial resolution via use of a nanosecond MIR pump laser in conjunction with an ultrahigh-speed complementary metal-oxide-semiconductor (CMOS) camera.

Figure 1a shows the electronic and optical components at the heart of wIR-PHI. A pulsed optical parametric oscillator MIR laser (M^2, Firefly, 2,270 MW m^{-2}) generates 1450 cm^{-1} pulses at 20 kHz. The infrared pulses are focused onto specimens using a reflective Schwarzschild objective (Ealing, 0.65 NA). A visible, continuous wave (CW) probe laser (532 nm, 166 MW m^{-2}) is simultaneously focused onto the same region using a high NA refractive objective (Nikon, 0.95 NA). Pump and probe beams are oriented in a counterpropagating geometry (**Figure 1b**) to maximize wIR-PHI's spatial resolution. Widefield excitation is achieved by first focusing the probe beam onto the back aperture of the objective to create a 20 ∝m^2 widefield spot. Scattered probe light is then collected with the same refractive objective and is ultimately focused onto the image sensor of a high-speed CMOS camera (Photron), whose frames are synchronized with the pump laser's MIR pulses via a digital delay generator.

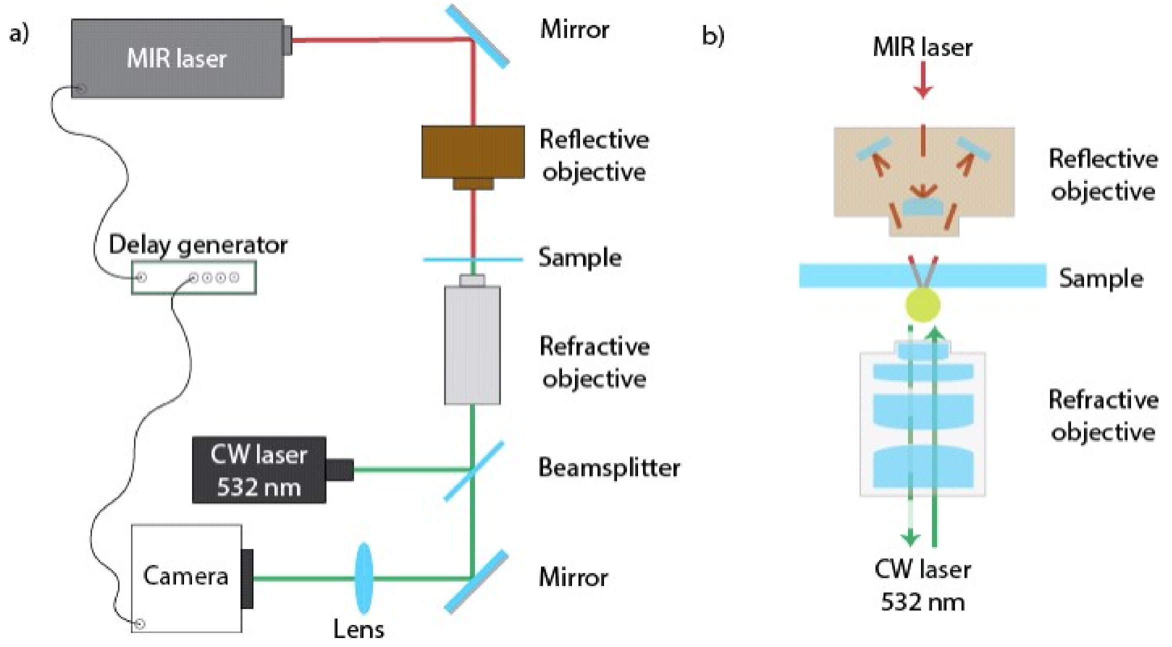

Figure 1. (a) Schematic of the wIR-PHI experimental setup, including MIR pump laser, 532 nm probe laser, high speed CMOS camera, and digital delay generator to synchronize pump pulses and camera frames. (b) wIR-PHI counterpropagating pump and probe geometry.

3. wIR-PHI VERSES IR-PHI

wIR-PHI is benchmarked to traditional IR-PHI using commercial, polystyrene nanoparticles (Phosphorex). Measurements and images focus on absorption at 1450 cm^{-1} due to polystyrene's CH_2 bending mode.[5] Particle diameters have been estimated via scanning electron microscopy (SEM) and reveal an average particle diameter of d=1028±43 nm. **Figure 2a** shows a representative SEM image of the studied ensemble along with a resulting sizing histogram.

Figures 2b,c now show resulting wIR-PHI (**Figure 2b**) and IR-PHI (**Figure 2c**) images of the same (individual) polystyrene nanoparticle. Both images cover the same ~5 ∝m^2 region. Whereas the wIR-PHI image was acquired in 4 seconds, the associated IR-PHI image required 20 minutes of raster-scanning. A 300-fold reduction in data acquisition time is observed with wIR-PHI. This illustrates the dramatic data parallelization achieved using a widefield, CMOS-based modality. A comparison of images also shows comparable wIR-PHI and IR-PHI signal-to-noise ratios.

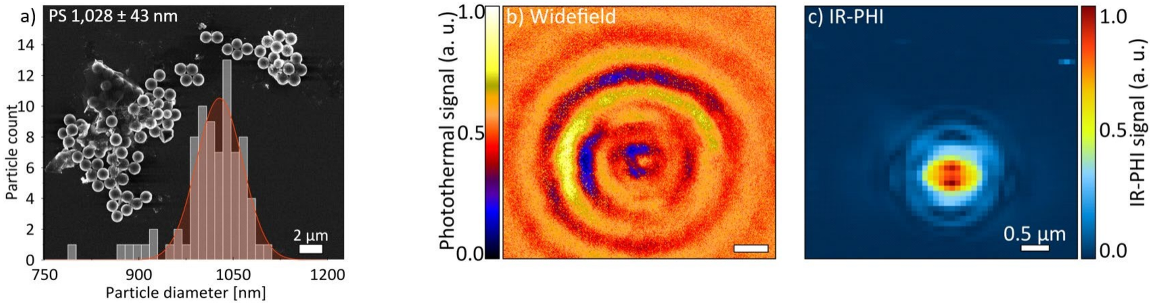

Figure 2. (a) SEM image of representative polystyrene nanoparticles studied. Inset: corresponding sizing histogram. (b,c) wIR-PHI and IR-PHI images of the same individual polystyrene nanoparticle. Scale bar 0.5 ∝m in both cases.

4. CONCLUSION

Infrared photothermal heterodyne imaging is an ultrasensitive technique that achieves super-resolution, infrared imaging throughout the MIR "fingerprint" region of the spectrum. By introducing a high speed CMOS camera, it becomes possible to parallelize data acquisition to realize an ultrafast, widefield IR-PHI modality. The developed wIR-PHI technique exhibits image fidelity to traditional IR-PHI. More importantly, it results in a 300-fold reduction in imaging time. Because CMOS camera frames are synchronized to MIR pump laser pulses, it is also possible to realize transient imaging of chemical species on the ns timescale.

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