Ultrastable long-duration super-resolution Raman microscopy

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Abstract

Near-field Raman microscopy utilizes nanoscale near-field light generated at the apex of a metallic probe to perform Raman imaging of chemical properties of samples with nanoscale spatial resolution (~10 nm). In this study, we developed an ultrastable near-field Raman microscope capable of extended measurement durations. In previous works, mechanical drift limited measurement times to around 30 minutes. By developing an automated drift compensation system, we realized a near-field Raman microscope ideally capable of imaging without any limitation to the measurement time. We demonstrated near-field Raman imaging of two-dimensional material MoS2 (molybdenum disulfide) over a 6-hour span.

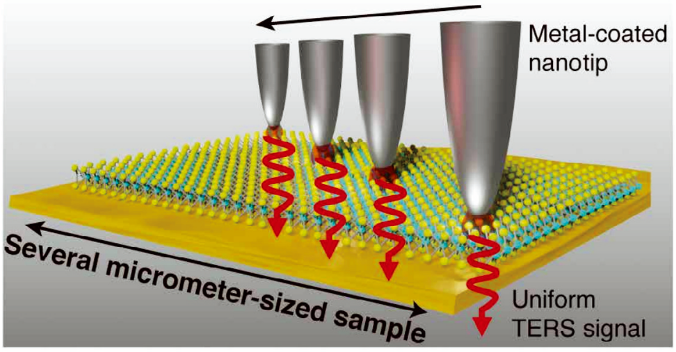
Background & Results

Near-field Raman microscopy, a powerful super-resolution microscopy technique, detects Raman scattered light from samples with about 10 nm spatial resolution, using near-field light generated at the apex of a metallic probe tip by illuminating it with incident light. Raman scattered light possesses rich optical and chemical information, such as molecular vibrations and chemical bonding. Super-resolution Raman imaging is possible by raster-scanning the sample. However, even a slight drift from the focal spot of the incident light can cause the near-field light to vanish. Imaging time is therefore limited to roughly 30 minutes until this drift occurs, which also restricts the observation area to only about 1 μm^2. This not only decreases measurement stability and reproducibility but also limits the samples that can be observed.

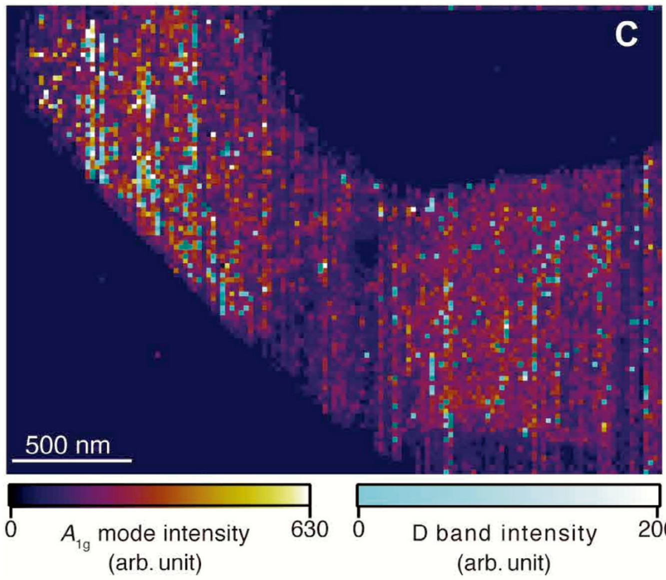
In this research, we developed a unique compensation system that three-dimensionally holds the metallic probe tip at the center of the focal spot with nanoscale precision, achieving an ultrastable near-field Raman microscope. To hold the tip within the focal spot, drifts in both the lateral and vertical directions need to be corrected. We introduced a galvanometer scanner for detecting and correcting tip drift in the lateral direction by obtaining scattering images from the probe tip within a certain period of time. For the vertical direction, we introduced a guide laser to detect vertical drift of the focus spot in terms of a lateral displacement of the guide laser on a position sensor, correcting it with an objective lens positioner. Using the developed compensation system, we confirmed that the Raman signal did not degrade even after much longer than 30 minutes. In addition, we successfully demonstrated super-resolution Raman imaging of the two-dimensional material MoS2 on a microscale area over 6 hours. This comprehensive large-area observation even enabled us to detect rare Raman signals (distributed in 0.2% of the entire area) originating from defect structures, which could be overlooked with precious methods.

Significance of the research and Future perspective

Previously, due to time constraints, only a very narrow area of the sample within a few hundred nanometers could be observed with the near-field Raman microscope. With high stability and an extended imaging period, we can now comprehensively image and analyze, for instance, micro-sized semiconductor transistors at the device scale. Furthermore, it holds the potential to observe biological samples that could not be easily imaged due to weak Raman signals. Importantly, the high stability and reproducibility significantly enhance its reliability and practicality. As a truly practical super-resolution Raman microscope, it offers contributions ranging from advanced materials to life sciences.



Overview of ultrastable near-field Raman Spectroscopy



Large-area super-resolution Raman image obtained of MoS_2 through 6-hour imaging

Patent

Treatise
Kato, Ryo; Moriyama, Toki; Umakoshi, Takayuki et al. Ultrastable tip-enhanced heperspectral optical nanoimaging for defect analysis of large-sized WS_2 layers. Science Advances 2022, 8, eabo4021. doi: 10.1126/sciadv.abo4021
Umakoshi, Takayuki; Kowashima, Koji; Moriyama, Toki et al. Tip-enhanced Raman spectroscopy with amplitude-controlled tapping-mode AFM. Scientific Reports 2022, 12, 12776. doi: 10.1038/s41598-022-17170-7

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Keyword near-field optical microscopy, Raman spectroscopy, super-resolution Raman microscopy