



Title	Development and applications of tip-enhanced Raman spectromicroscopy
Author(s)	加藤, 遼
Citation	大阪大学, 2021, 博士論文
Version Type	
URL	https://hdl.handle.net/11094/82216
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論文内容の要旨

氏 名 (加 藤 遼)	
論文題名	Development and applications of tip-enhanced Raman spectromicroscopy (チップ増強ラマン顕微鏡の開発とその応用)
論文内容の要旨 Tip-enhanced Raman spectroscopy (TERS) is a powerful nanoscale analytical technique that provides both chemical and topographic properties of materials at nanoscale since it is benefited from plasmon-enhanced Raman spectroscopy and scanning probe microscopy (SPM). Owing to the high sensitivity and high spatial resolution, TERS has been leveraged to characterize chemical properties of nano-structured materials, such as nano-carbon materials, semiconductors. However TERS has not been yet recognized as a reliable and practical analytical tool because of several critical issues. General goal in this thesis is improving TER spectromicroscopy and demonstrating its applications to make TERS more reliable and prevalent analytical tools. In this dissertation, several research projects on TERS analysis as well as instrumentation are presented in order to address the issues in TERS. Beginning from the Chapter 1, fundamental of Raman spectroscopy, plasmonics for enhanced spectroscopy and TERS is introduced. Subsequently, earlier work as well as cutting-edge work on TERS is highlighted. From Chapter 2 to 4, TERS analysis of unique properties of nano-structured materials is presented. In Chapter 2, the capability of TERS was extended into characterizing nanoscale heterogeneities on the surface of MoS₂, such as nano-defects and wrinkles. Owing to chemical specificity with nanometer spatial resolution and layer-sensitive vibrational modes of MoS₂, we revealed the presence of nanoscale heterogeneous structures by TERS imaging. In Chapter 3, nanoscale analysis of interwall interactions in carbon nanotubes and the numerical calculation method for TERS intensity of the defect mode from MWNTs are discussed. In Chapter 4, the methodology for gap-mode TERS measurement of the biological sample, lipid bilayer systems, was discussed. Chemically synthesized gold nanoplatelets were utilized as plasmonic substrates for gap-mode TERS measurement of supported lipid bilayers. Chapter 5 describes new approach of TERS for nano-absorption imaging, where a silicon nano-tip instead of a metallic nano-tip, was used to observed absorption properties of materials. Nanoscale characterization of absorption coefficient of two types of carbon nanotubes was demonstrated by measuring the intensity of Raman scattered signal of silicon, which is the base material of an AFM cantilever tip. Chapter 6 focuses on instrumentation of three dimensional drift compensation system in TERS microscopy and demonstration of robust TER-nanospectroscopy. The 3D drift compensation system was developed to maintain strong plasmonic fields at the apex of a metallic probe tip. Developed system enabled to perform long-term, large-area and high-resolution TERS imaging. Chapter 7 describes fabrication of TERS probe tips to achieve highly reproducible TER nanospectroscopy. Highly reproducible TERS probe, termed “one-side metal-coated pyramidal cantilever tips” for gap-mode TERS was introduced. Gap-mode TERS measurement with 100% reproducibility was demonstrated. Besides, an interesting application using the one-side metal coated tip is also discussed, where chemically modified tips allow to map optical fields of metallic nano- structures. A general conclusion and perspective is presented in Chapter 8 to recap this dissertation.	

論文審査の結果の要旨及び担当者

氏 名 (加 藤 遼)			
論文審査担当者		(職)	氏 名
	主 査	教授	バルマ プラブハット
	副 査	教授	高原 淳一
	副 査	教授	菅原 康弘
	副 査	准教授	久保 若奈 (東京農工大学大学院工学研究院先端電気電子部門)

論文審査の結果の要旨

This dissertation focuses on the development and applications of tip-enhanced Raman microscopy. This powerful nanoscale analytical technique, which is based on tip-enhanced Raman spectroscopy (TERS), provides both chemical and topographic properties of materials at nanoscale. It utilizes a sharp metallic nanotip, which is illuminated with incident light to generate a strong and nanometrically confined light field at the apex of the nanotip that amplifies Raman scattering of molecules located directly underneath the apex of the nanotip, providing a true nanoscale resolution to optical microscopy. Owing to the high sensitivity and high spatial resolution, TERS microscopy has been utilized to characterize chemical properties of several types of nano-materials. However, TERS has not yet been recognized as a common and practical analytical tool. This is because of several critical issues that TERS still suffers from. One of the major issues is the reproducibility of enhancement, typically about 20-50%, which mostly depends on the reproducibility of the metallic nanotip. Another critical issue is thermal and vibrational drift of TERS system, which makes it unreliable for regular characterization. These shortenings have so far limited the application of TERS-based microscopy, where only certain samples with certain properties have been investigated, mostly in order to demonstrate the strength of the technique, rather than utilizing it for common analysis.

This dissertation presents a comprehensive study on TERS and TERS-based microscopy, where it takes the challenges of bringing the reproducibility to 100%, and stabilize the nanoscale drifts to a level where measurements of several hours could be performed without any significant drift. At the same time, it shows some new applications and future direction of TERS-based microscopy. Main points of the research in this dissertation are described below.

- First, this dissertation discusses the instrumentation for a 3D drift compensation system in TERS microscopy. The 3D drift compensation system is developed to maintain strong plasmonic fields at the apex of a metallic probe tip. It is demonstrated through the developed system that a long-duration (about 6 hours) and large-area (several tens of micrometers) high-resolution TERS imaging is possible.

- By utilizing one-sided metal coating on a pyramidal cantilever tip and using it in the so-called gap-mode TERS, a 100% reproducibility of TERS enhancement is demonstrated. Besides, an interesting application of this tip is discussed, where chemically modified tips could be used to map optical fields of metallic nano-structures.

- On the application side, this dissertation investigates nanoscale heterogeneities, such as nano-defects and wrinkles, on the surface of MoS₂. Owing to chemical specificity with nanometer spatial resolution and layer-sensitive vibrational modes of MoS₂, it reveals the presence of nanoscale heterogeneous structures by TERS imaging. In another interesting application, it demonstrates a nanoscale analysis of interwall interactions in a multi-walled carbon nanotube and confirms the results through a numerical calculation. It further discusses a methodology for gap-mode TERS measurement of biological samples, particularly the lipid bilayer. Chemically synthesized gold nanoplatelets are utilized as plasmonic substrates for gap-mode TERS measurement of lipid bilayers. Finally, a very interesting application through a new approach of TERS microscopy is discussed where a TERS-based nano-absorption imaging of two different kinds of carbon nanotubes is demonstrated. Here, instead of a metal-coated nanotip, a bare silicon nanotip is used to observed absorption properties. Nanoscale characterization of absorption coefficient of two types of carbon nanotubes is demonstrated by measuring the intensity of Raman scattered signal of silicon, which is the base material of the nanotip.

Overall, this dissertation shows great potential of TERS-based microscopy through certain developments and improvements. It further demonstrates several new applications to confirm the versatility of TERS and its potential to become a regular nanoscale optical characterization tool for several materials. The referees found consistent consideration and strategy to demonstrate the strength of TERS and TERS-based nanoimaging, which is yet not so well explored, through certain important developments of the technique. Therefore, the referees have accepted that this dissertation has remarkable achievements and it deserves a doctoral degree.