



Title	Polarization-controlled tip-enhanced Raman spectroscopic imaging
Author(s)	三野, 聡大
Citation	大阪大学, 2015, 博士論文
Version Type	
URL	<a href="https://hdl.handle.net/11094/52158">https://hdl.handle.net/11094/52158</a>
rights	
Note	やむを得ない事由があると学位審査研究科が承認したため、全文に代えてその内容の要約を公開しています。全文のご利用をご希望の場合は、<a href="https://www.library.osaka-u.ac.jp/thesis/#closed">大阪大学の博士論文について</a>をご参照ください。

*The University of Osaka Institutional Knowledge Archive : OUKA*

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

## 論文内容の要旨

氏 名 ( 三 野 聡 大 )	
論文題名	Polarization-controlled tip-enhanced Raman spectroscopic imaging (偏光制御した先端増強ラマン分光ナノイメージング法の開発)
<p>In this thesis, I presented a detailed discussion of polarization in tip-enhanced Raman spectroscopy (TERS) for the first time. TERS identifies molecular vibration from the frequency of Raman scattering light at extremely high spatial resolution, far beyond the diffraction limit of light. When the polarization is precisely controlled, one can moreover reveal the variation of molecular orientation and symmetry at the nanoscale, since different Raman modes that are sensitive to the polarization are selectively excited. The abundance of information given by the polarization-controlled TERS will certainly lead to better understanding of nano material, and contributes to the development of future nanoscale science.</p> <p>In the 1st chapter of this dissertation, I started from explaining the significance of polarization in Raman spectroscopy, and then, presented basics of polarization-controlled Raman (<i>p</i>-Raman) spectroscopy. After an overview of applications of <i>p</i>-Raman spectroscopy was given, I argued that the higher spatial resolution and the flexible controllability of polarization are going to be needed.</p> <p>In the 2nd chapter, polarization control technique in far-field spectroscopy was introduced especially with a focus on the control with a spatial light modulator (SLM) which is developed in recent years. Utilizing the SLM, I developed a <i>z</i>-polarization Raman microscope which realized polarization measurements in the direction normal to a substrate with a high <i>NA</i> objective lens. Molecular orientations in pentacene thin films were successfully analyzed by using the microscope.</p> <p>In the 3rd chapter, I provided an overview of TERS. The super spatial resolution of TERS can be achieved by confining and enhancing light field in close proximity to the apex of a sharp, metallic tip. I presented that TERS imaging gave rich information to understand the property of a nanomaterial.</p> <p>In the 4th chapter, the main point of this thesis, the polarization property of a TERS tip was discussed. Neither evaluation nor control of the polarization properties of near-field light in TERS is as straightforward as in usual far-field illumination, because the metallic random nanostructure of the tip apex affects the near-field polarization. The variation in the polarization property from tip to tip was evaluated by measuring the pattern of light scattering by the tip apex. I showed the first polarization-dependent TERS images of single-walled carbon nanotubes, which convinced that near-field polarization was precisely understood by my evaluation technique.</p> <p>In the 5th chapter, I finally introduced polarization control in TERS. The polarization control was achieved by modifying the incident polarization with consideration for the unique polarization property of a given tip. I succeeded in exciting a particular vibration at the nanoscale by use of the near-field polarization control technique.</p> <p>At the end, I wind up the thesis by giving the conclusion of my work.</p>	

## 論文審査の結果の要旨及び担当者

氏 名 ( 三 野 聡 大 )			
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	井上 康志
	副 査	教授	高原 淳一
	副 査	教授	二又 政之 (埼玉大学 理工学研究科)

## 論文審査の結果の要旨

This dissertation describes polarization in tip-enhanced Raman spectroscopy (TERS) in great detail for the first time. This work is important and interesting in nanoscience and technology, since polarization in TERS gives new information related to molecular symmetry and orientation at the nanoscale. Main specific achievements discussed in this dissertation are summarized as below.

- The experimental method to investigate polarization of near-field light was established. There currently exists no experimental method to determine the status of near-field polarization for a given tip used in TERS. In this dissertation, the near-field polarization was analyzed from the direction of dipole oscillation excited at the tip apex which was identified by measuring the scattering pattern produced by a metallic tip using the technique of defocused imaging. Variation in near-field polarization from tip to tip was clearly observed, which proved that the evaluation technique of near-field polarization was indispensable for polarization analysis in TERS.
- Polarization-dependent TERS imaging was successfully achieved. TERS images of carbon nanotubes were constructed by using three different tips after the near-field polarization around the apex of the tip was investigated. Contrast of the TERS images clearly varied as predicted from the near-field polarization. Moreover, excellent agreement between the TERS images and calculated images ensured that polarization analysis in TERS was quantitatively performed owing to the method mentioned above.
- Finally, the control of polarization of near-field light was demonstrated. By adjusting incident polarization with consideration for the unique polarization property of a tip, near-field light polarized in an arbitrary direction was generated. The control technique enables to adapt polarization of near-field light to a sample, enhancing the versatility of polarization TERS imaging.

Thus, the dissertation presents new aspect of polarization in TERS which has potential to contribute to the better understanding of nanomaterials. Also, results are well supported both experimentally and analytically, convincing referees of the author's conclusion. For these reasons, the referees accepted that this dissertation reached the level high enough to grant a doctoral degree.