Form 3

Abstract of Thesis

Name	(CHAUNCHAIYAKUL SONGPOL)
Title	Nanoscale Investigation of Optical Activity of Chiral Molecular Systems by STM-TERS (STM探針増強ラマン分光法を用いたキラル分子系のナノスケール光学活性評価)

Abstract of Thesis

Chiral molecules are those with molecular structures which cannot be superimposed on its mirror image. It is especially important in life sciences, since many biologically-active molecules are chiral. Although they have been studied since long ago, the origin of the imbalance of chirality in nature still remains a mystery to this day. Nevertheless, the concept of chirality is extremely important to biological systems. For example in the field of pharmacy, a drug can be both cure and poison, depending on which enantiomer is consumed. Thus, to understand the emergence of chirality from the single-molecular scale would be highly beneficial to mankind. By far the only way to distinguish enantiomers is by observing its optical activity. However, conventional spectroscopic methods are restricted by the optical diffraction limit, prohibiting one from studying optical activity truly from single molecules.

Therefore, this dissertation reports the possibility of the detection of single molecule optical activity by means of tip-enhanced Raman spectroscopy (TERS), which relies on the near-field enhancement effect due to surface plasmon resonance at the tip apex. A Raman spectrometer was equipped to a custom-built scanning tunneling microscopy (STM) system. The excitation channel of the laser was modified to include a quarter-waveplate retarder, so as to excite the STM tip with circularly-polarized light (CPL). Using this setup, the Raman scattering of the chiral sample can be enhanced by the TERS effect induced by left- and right- CPL. The Raman optical activity (OA) of the the sample can then be measured from the intensity difference of the output Raman scattering signal.

To evaluate the performance of this system, the ideal reference must exhibit strong optical activity, as well as be able to withstand the effect of laser irradiation during the course of TERS experiments. In this dissertation, two test samples were chosen: helicene derivatives, and single-walled carbon nanotubes (SWNTs).

Helicene derivatives were chosen for their strong optical activity, and are also known to form a self-assembled monolayer on metallic surfaces, which is an ideal test sample for TERS. In chapter 4 of this dissertation, the self-assembly formation of M-type helicenediols was investigated. It was found that a heated substrate during molecule deposition facilitates the formation of self-assembly, in comparison to substrates maintained at lower termperatures. The molecules formed highly ordered islands surrounded by disordered regions. Scanning tunneling spectroscopy measurements revealed that the HOMO and LUMO peaks at -1.7 and 2.2 V in the case of single molecules and disorder regions. On the self-assembled twin rows structure, an additional peak was observed -2.45 V. The difference in the electronic structures was ascribed to the different degrees of molecule-molecule interaction and molecule-substrate interaction. It can be concluded that intermolecular interaction is dominant in the self-assembled islands, whereas molecule-substrate interaction is dominant in the disordered region. When the same fabrication procedure was applied to a sample consisting of a racemic mixture of helicenedialdehyde molecules, the self-assembly formation also occured. A TERS spectrum was successfully obtained on the racemic sample. Such a chiral surface comprising both enantiomers is a promising reference sample for the investigation of OA by TERS, subject to further optimization of experimental conditions.

The carbon nanotube (CNT) has become a classic test sample for TERS systems, owing to its robustness for long durations under laser irradiation, and well-known Raman scattering modes. It is also well-known that the CNTs properties can be predicted by its chiral vector. However, less is known that the chiral vector can be rolled

in two directions, each resulting in a CNT of similar chiral indices but with opposite handedness. The handedness of chiral CNTs and their optical activity has not been studied until recently, when researchers have been able to extract the CNTs by handedness using molecular chiral recognition. In this study, the properties of individual CNTs were investigated by using TERS. Some nanoscale properties, such as the quantum interference effect between Raman scattering pathways, the localization of the D band at the end of a SWNT were observed. When irradiated by left- and right-CPL, a circular intensity difference was observed. The TERS mapping, excited by CPL, also showed a larger circular intensity difference on the CNT in comparison to the substrate areas, which indicates optical activity when the tip is above the CNT. Such optical activity is possibly due to the optical selection rules owing to the handedness of the CNT itself, or optical activity due to the tip geometry, or errors due to the measurement system, or all of the above combined. Nevertheless, it can be stated that near-field optical activity relevant to the CNT was detected. To further sophisticate the results, it is necessary to correlate the OA signal with the CNT handedness, by atomic resolution imaging.

The results in this dissertation show that this new branch of TERS can possibly be used in the study of chiral molecules in the nanoscale, which could lead to an understanding of the origin of chirality itself. Such a fundamental piece of knowledge could potentially lead to valuable applications in the field of biology, pharmacy, and life sciences, which would be of great benefit to mankind.

様式７

論文審査の結果の要旨及び担当者

氏　名	（CHAUNCHAIYAKUL SONGPOL）		
論文審査担当者		（職）	氏　名
	主 査	教授	桑原　裕司
	副 査	教授	森川　良忠
	副 査	教授	バルマ　プラバット
	副 査	准教授	齋藤　彰

論文審査の結果の要旨

本論文の要旨は、新規に構築した走査トンネル顕微鏡探針増強ラマン分光法（STM-TERS）を用いて、ラマン信号の光学非対称性を評価することにより、固体表面上に吸着したキラル分子系の対掌性、及びカーボンナノチューブ（CNT）の螺旋方向の違いを区別したことにある。

キラリティとは、鏡像体が、自身と重ならない性質をいう。片方の対掌性のみを有する、すなわち一方のみの鏡像異性体（エナンチオマー）で構成される生体分子は、ホモキラリティ現象としてよく知られているが、その起源は未だ謎のままである。化学的、物理的性質が同一である光学異性体の区別は、左右円偏光への応答性の違いでのみ検出されうる。しかしながら、プローブ光の光学的回折限界から、検出波長よりも小さい領域すなわちナノスケール実空間観察はなされていない。これらの回折限界を突破するための検出手法として、著者は、STM をベースにした TERS 装置を立ち上げ、さらにそれを用いて、キラル有機分子であるヘリセン誘導体、及びカーボンナノチューブの局所電子・振動状態及び光学非対称性を評価している。

ヘリセン誘導体は、その特異な螺旋構造から、強い光学非対称性を持つ分子として知られる。また、固体表面上で自己組織化構造を容易に形成することにより、その安定した構造から分子配列および分子配向を評価可能である。本論文では M タイプ（左ねじ方向のらせん構造を持つ）のヘリセン誘導体について、自己組織化構造形成に伴う電子状態および振動状態の変化を詳細に評価している。走査トンネル分光法により、分子の HOMO 及び LUMO に起因するピークを確認し、また自己組織化構造形成において、分子間相互作用により HOMO-LUMO ギャップ内に新たな電子準位が形成されることも見出している。一方 TERS 測定では、ヘリセン誘導体に起因する分子振動をナノスケールの空間分解能で検出することに成功している。

CNT は、TERS 計測において、これまで多くの研究例があり、詳細にその振動状態が解析されてきた。本研究では、従来の TERS システムに円偏光レーザーを組み込むことにより、CNT の局所振動状態解析、及び世界で初めて光学非対称 TERS 計測をおこなっている。まず、多層カーボンナノチューブにおいて、その巻き数と、G バンドと 2D バンドのピーク強度比（I(2D)/I(G)）との関係を評価し、その結果、巻き数と I(2D)/I(G)が、ほぼ比例関係にあることを見出している。この結果から、多層カーボンナノチューブ層間の相互作用が、ランダムに相互作用する多層グラフェンシートと類似していると結論し、ピーク強度比から直接多層 CNT の総数の見積もりが可能であることを初めて明らかにしている。一方で、光学非対称 TERS 計測により、STM 探針直下の単層 CNT について、左右円偏光に対するピーク強度を直接計測・比較している。その結果、右円偏光及び左円偏光入射に対するラマン散乱ピーク強度比が大きく異なることを示し、それが、観察する CNT の右巻き・左巻きを区別することに利用できることを初めて示している。

以上のように、本論文は従来の TERS 計測法に対して、光学活性評価を可能にする光学非対称 TERS システムを新たに構築し、固体表面に吸着した有機分子及び CNT の対掌性を評価したものである。本研究で得られる情報は、今後、生体分子解析、薬剤創製プロセス、さらには生命科学研究に対して、基本的且つ重要な情報を提供するものと強く期待される。

よって本論文は博士論文として価値あるものと認める。