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针尖增强拉曼/荧光体系光学特性研究

Studies on optical properties of tip-enhanced Raman/fluorescence system

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Studies on optical properties of tip-enhanced Raman/fluorescence system

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摘 要

针尖增强拉曼光谱（Tip-enhanced Raman spectroscopy，TERS）和针尖增强荧光（Tip-enhanced fluorescence，TEF）具有极高的检测灵敏度和空间分辨率，已经成为表面科学研究中强大的表征手段。尽管 TERS 及 TEF 在近年取得了重大的进步，但依然存在许多重大的科学问题尚待解决。如 TERS 实验中实现的亚纳米空间分辨理论机制已不能用常规的局域电场增强理论来加以解释；进展迅速的 STM-TERS 技术受到样品和基底导电的严重限制而急需发展普适性更广泛的针尖增强拉曼体系;如何设计和发展高分辨多功能纳米光谱仪器平台实现 TERS 和 TEF 的原位精确测量，实现两种光谱手段在研究中的优势互补。与此同时，通过探索 TERS 和 TEF 的定向发射特性与针尖、基底以及分子等因素间的定量关系，实现 TERS 和 TEF 信号收集效率和检测灵敏度的大幅提高具有十分重要的科学意义和实际应用价值。针对 TERS 和 TEF 研究中上述问题，我们对针尖增强拉曼/荧光体系光学特性展开了研究。

本论文共分为六部分。前言部分介绍表面等离激元相关理论和应用，概述 TERS 和 TEF 技术的主要特点及研究现状，并在此基础上提出本论文的主要设想及思路。第二章着重介绍主要的数值方法：三维时域有限差分法（Three-dimensional finite-difference time-domain，3D-FDTD）和有限元法（Fimite element method，FEM）。第三章，从理论上定量研究了 AFM-TERS 体系的光学性质与针尖、基底及激发光等因素的具体关系，并初步进行了实验研究。第四章，从理论上定量探讨了 STM-TERS 体系的电场和电场梯度增强，重点解决了亚纳米 TERS 空间分辨率的物理机制问题。第五章，定量研究了 STM-TERS 体系和 STM-TEF 体系的拉曼增强和荧光增强，重点解决分子拉曼和荧光信号的原位精确测量问题。第六章，定量研究了 STM-TERS 体系和 AFM-TEF 体系的定向发射特性，为提高分子信号的收集效率和检测灵敏度提供可靠的理论依据。

本论文工作的创新点及主要研究成果如下：

1. 理论设计高增强因子、高空间分辨的 AFM-TERS 体系并初步加以实验证实。利用 3D-FDTD 方法，通过优化设计针尖、激光以及基底，TERS 增强因子可以高达 9 个数量级，空间分辨率可以提高到 2.5 nm。初步实验结果证明，当金层厚度在 60-80 nm 之间时，TERS 信号强度最大，与理论预测吻合很好。该理论

计算不仅对 AFM-TERS 物理机制的理解具有一定的帮助，而且能够为构建高效可行的 AFM-TERS 仪器提供理论指导。

2. 利用电场梯度效应解释 TERS 极高空间分辨率。虽然亚纳米 TERS 空间分辨率已在实验上得到实现，但其物理机制仍处于激烈的讨论中。在此，利用 FEM 方法研究了 STM-TERS 体系中的电场及电场梯度增强，得到了电场增强与针尖锥角的定量关系以及特定锥角下的电场和电场梯度分布。计算结果表明，电场梯度对 TERS 空间分辨率同样具有非常重要的作用，特别对于水平吸附在基底上的探针分子来说，电场梯度将发挥主导作用。该理论工作提出了一种新的物理机制来解释亚纳米 TERS 分辨率，对进一步理解 TERS 机理具有一定的参考价值。

3. 提出并优化设计针尖-基底体系，实现 TERS 和 TEF 的原位精确测量，发展高分辨多功能纳米光谱技术。利用 3D-FDTD 方法，分别定量研究了 STM-TERS 和 STM-TEF 体系的拉曼增强和荧光增强与针尖-基底距离的定量关系。计算结果表明，能够实现 TERS 和 TEF 的原位精确测量的最优针尖-基底间距为 2 nm，此时，TERS 分辨率高达 3.5 nm，荧光光谱的分辨率达到 10 nm 左右。该理论结果，为构建高效的高分辨多功能仪器平台具有一定的指导意义。

4. 探究 STM-TERS 及 AFM-TEF 体系的定向发射特性，提高信号收集效率和检测灵敏度。利用 3D-FDTD 方法，分别研究了 TERS 和 TEF 远场散射信号与针尖、分子及激发光等因素的定量关系。计算结果表明，TERS 和 TEF 信号在三维空间具有很好的定向发射特性，并且利用该特点能够有效提高信号收集效率及检测灵敏度。该理论工作不仅能够加深对定向发射机制的理解，而且能够指导 TERS 和 TEF 平台的构建。

关键词：表面等离激元；针尖增强拉曼光谱；针尖增强荧光；表面等离激元共振

Abstract

Tip-enhanced Raman spectroscopy (TERS) and tip-enhanced fluorescence (TEF) with ultra-high detection sensitivity and spatial resolution have been powerful characterization techniques in the study of surface science. Although TERS and TEF achieve significant progress in recent years, there are still many unsolved major scientific issues. For example, the conventional localized electric field enhancement theory is not enough to completely explain the physical mechanism of the sub-nanometer spatial resolution achieved in TERS expetiments; Because the rapid-developed STM-TERS is severely limited by the conductivity of the sample and the substrate, it is urgent to develop tip-enhanced Raman system with more general universality；How to design and develop the muti-functional nano-spectroscopy instrument platform with ultra-high spatial resolution, and thus helps integrate the advantages of the two spectroscopy techniques in process of research. Meanwhile, it has great scientific significance and practical application value to explore the quantitative relations between the optical properties of TERS/TEF and the tip, substrate as well as the molecule and so on, and thus largely improve the collection efficiency and detection sensitivity of TERS and TEF. To cure the above involved problems in TERS and TEF, we theoretically studied the optical properties of tip-enhanced Raman and fluorescene systems.

The thesis is divided into six chapters. In the first chapter, the purpose and main tasks of this work were proposed after reviewing the basic theory and the extended applications of surface plasmons (SPs), the main features and the progress of TERS and TEF techniques. In the second chapter, three-dimensional finite-difference time-domain (3D-FDTD) and fimite element method (FEM) were basically described. In the third chapter, we theoretically studied the quantitative relations between the optical properties of the AFM-TERS and the influence factors, such as the size and material of the tip, the thickness of metal coating and so on. The preliminary experiments were performed. In the fourth chapter, we theoretically studied the localized electric field enhancement and electric field gradient enhancement in the STM-TERS, and provided a possible physical mechanism of sub-nanometer spatial resolution. In the fifth chapter, the Raman and fluorescence enhancement in STM-TERS and STM-TEF, respectively, were theoretically investigated to realize the

in situ measurement of molecular Raman and fluoresncence which is very important for the development of multi-functional nano-spectroscopy instrument combining TERS and TEF. In the sixth chapter, we quantitatively studied the spatial distribution of directional emission in STM-TERS and AFM-TEF systems, respectively, which is can provided reliable theoretical references for improving the collection efficiency and optimizing the configurations.

The innovative points and key research results are as follows:

1. Theoretical design and experimental demonstration of AFM-TERS system with high enhancement factor and spatial resolution. 3D-FDTD calculations demonstrate that the TERS enhancement factor can be tuned to as high as 9 orders of magnitude, and the spatial resolution could be down to 2.5 nm, by optimizing the tip, excitation laser, and the substrate. Preliminary experimental results for AFM tips coated with gold layer of different thickness, reveals that the maximum enhancement can be achieved when the thickness is about 60-80 nm, which is in good agreement with the theoretical predictions. Our results not only provide an understanding of the underlying physical mechanism of AFM tip-based TERS, but also guide the rational construction of a working AFM-TERS system with high efficiency.

2. Explaining the ultra-high TERS spatial resolution by electric field gradient effect. Although the tip-enhanced Raman spectroscopy (TERS) with sub-nanometer spatial resolution has been recently demonstrated experimentally, the physical mechanism underlying is still under discussion. Here, FEM was used to investigate the electric field gradient effect of STM-TERS system and we obtained the quantitative relation between the electric field enhancement and the cone angle of the tip. We also get the the spatial distributions of electric field and its gradient field. Our calculations suggest that the ultra-high spatial resolution of TERS can be partially attributed to the electric field gradient effect. Particularly, in the case of TERS of flat-lying molecules，we find the electric field gradient enhancement is the dominating factor for the high spatial resolution. Our theoretical study offers a new paradigm for understanding the mechanisms of the ultra-high spatial resolution demonstrated in tip-enhanced spectroscopy which is of importance to understand the TERS mechanism.

3. Proposing and optimally designing tip-substrate system to realize the in-situ