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界面等离激元模式及其应用研究

Studies on Plasmonic Modes at Interfaces and Their Applications

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Studies on plasmonic modes at interfaces and their applications

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By

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摘 要

近年来，表面等离激元(Surface Plasmons, SPs)广泛应用于生物、化学、表面科学、材料科学以及能源等领域。在 SPs 相关领域取得重大突破的同时，仍存在诸多亟待解决的问题。如：新型表面增强光谱技术中的增强机理问题；进一步提高光谱空间分辨率的问题；复杂纳米结构（如：聚集体，界面纳米结构等）新型等离激元模式识别等问题。纳米结构中等离激元模式是一切等离激元光学性质的源头。因此，等离激元模式的识别及其光学性质分析在等离激元基础和应用研究中扮演着非常重要的角色。

本论文采取理论为主，实验为辅的方式对界面纳米体系中的等离激元光学性质展开研究，主要分成七部分。绪论部分系统地介绍了表面等离激元基础理论、相关应用、最新进展、并在此基础上提出本论文的主要设想和研究思路。第二章重点介绍了本论文借助的数值计算方法以及实验表征手段。第三章借助单个 Au@SiO_2 壳层隔绝纳米粒子-金膜体系系统地研究了壳层隔绝纳米粒子增强拉曼光谱的电磁场增强机理。第四章对纳米粒子多聚体-金膜体系的远近场光学特性进行探究。第五章选取周期性纳米阵列为研究对象，对法诺共振特性进行探究。第六章，通过理论与实验结合探究了粒子-电介质-金膜体系中等离激元磁共振的光学特性。第七章探究了石墨烯谐振器-金膜体系中等离激元声学模式的光学特性。本论文工作的主要工作及创新点如下：

1. 单粒子-金膜体系中的电磁增强特性研究。通过对单个 Au@SiO_2 壳层隔绝纳米粒子-金膜体系进行系统研究表明，在外电场偏振方向平行于基底平面时，粒子与金基底间仍可产生高的电场增强；1-2 nm 的 SiO_2 壳层可以有效地阻止粒子与基底间电子交换进而促进粒子与基底间的耦合效应。该理论为 SHINERS 实验提供了理论指导，有望促进 SHINERS 在表面科学领域的应用。

2. 纳米粒子多聚体-金膜体系中的“热点”可控转移。通过对该复杂体系的等离激元特性进行系统研究表明，受多处等离激元效应的影响，该体系中呈现出多个等离激元杂化模式。通过抑制或者促进某处的等离激元耦合效应可实现热点在粒子-粒子以及粒子-金膜两处间隙间的可控转移，这是存在于多聚体-金膜体系中普适规律。这项工作为纳米结构中实现热点可控提供了全新的研究思路。

3. 周期性纳米阵列中法诺共振特性研究。通过对周期性纳米结构中的模式耦

合特性进行系统研究表明，通过合理设计结构参数，可有效地调节局域等离激元模式与传播等离激元模式的耦合程度，从而诱导法诺共振的产生。得益于法诺共振特性，我们可得到高增强局域场，高折射率灵敏性以及高的传感品质因子。这一理论研究表明，法诺共振是有效提高表面增强光谱以及表面等离激元传感的敏感性的一种途径。

4. 等离激元磁共振增强拉曼光谱。通过采用理论和实验结合的方法，我们设计了一类可在可见光区实现等离激元磁共振且可进一步用于表面增强光谱的实用体系。理论计算和拉曼光谱实验研究表明，磁共振模式是该体系中最强的电磁场增强来源。这一结果是首次将等离激元磁共振用于表面增强拉曼光谱，有望推动等离激元磁模在增强光谱上的应用。

5. 声学等离激元模式光学特性探究。石墨烯等离激元由于具有连续可调、高局域场增强以及能量限域性等特点受到广泛关注。我们选取石墨烯圆盘-金膜体系为目标体系，系统地探究了该体系中声学等离激元模式的光学特性。较传统的光学模式而言，该体系中的等离激元声学模式具有更高的能量限域性以及场增强，这为石墨烯在光调制器、传感器、表面增强光谱等方面的应用提供了更佳的平台。

关键词：等离激元共振, 表面增强拉曼光谱，磁模，声学等离激元模

Abstract

For the past years, surface plasmons (SPs) has been widely applied in chemistry, biology, surface science, material science and energy. Although the SPs related-fields have made great progresses, there are still some issues to be solved urgently. For example, the electromagnetic field enhancement mechanism in some novel spectroscopy techniques. Further improving the space resolution. The identifications of the novel plasmons resonances in the complex nanostructures. Thus, analyzing the SPs resonant modes and the related optical properties are very important and urgent because they will not only provide theoretical guidance, but also significantly promote wide applications of SPs.

This thesis, which is developed by correlating the numerical methods with experimental approaches, studies the plasmonics properties of nanosystems at interfaces and can be divided into seven parts. The introduction part induces the fundamental, applications and newly development of SPs. Based on that, the purposes and main tasks of this thesis were proposed. In the second chapter, the numerical and experimental methods used in this work were basically described. In the third chapter, the electromagnetic enhancement mechanism in SHINERS is explored through studying the optical properties in the single shell-isolated nanoparticle (SHIN)-gold film system. In the forth chapter, the precisely controlled transfer of “hot spots” in multiple nanoparticle aggregates-gold film system was revealed. In the fifth chapter, the Fano resonance properties were studied in the periodic arrays. In the sixth chapter, the plasmonic properties of magnetic-like resonances were explored in the particle with large size-dielectric layer-gold film system. In the seventh chapter, we explored the properties of acoustic plasmons modes in graphene resonator-gold film system. The main contents and highlights are listed as follows:

1. The electromagnetic enhancement optical properties of single particle-gold film system. Based on the systematical investigation of single SHIN-gold film, the findings show that 1-2 nm SiO_2 shell can effectively stop the electrons exchange between particle and gold film; Under the polarization of incident light parallels with

the substrate plane, the "hot spots" with high enhanced field at the particle-film junction was revealed. These findings provide theoretical guidance for SHINERS, and promote the applications of SHINERS in surface science.

2. "Hot spots" controlled transfer in multiparticle-gold film configurations. Through systematically investigating the optical properties of multiparticle-gold film configurations, several SPR hybrid modes were revealed benefited from the complex plasmon coupling effects. By suppressing or promoting specific plasmon coupling effect, the position of "hot spots" can be precisely transfer between particle-particle and particle-gold film junctions. This is a general principle for multiparticle-gold film configuration. These findings significantly promote the development of SHINERS.

3. The investigation of Fano resonance properties in periodic arrays. The findings show that, the coupling degree between localized surface plasmons and propagating surface plasmons, which can be tuned by the structured parameter, plays the vital role in the happening of Fano resonance. The higher enhanced electric field, sensitivity and figure of merit (FOM) are obtained benefited from the Fano resonance. These findings imply that the Fano resonance is an effective way to increase the sensibility of surface enhanced spectroscopy and sensor.

4. Plasmonic magnetic resonances to enhance surface enhanced Raman spectroscopy. Combining with theoretical and experimental approaches, we designed a practical system to support magnetic resonances for enhanced surface spectroscopy. Our theoretical and experimental results imply that the magnetic mode is the optimal enhanced source, providing largest Raman signals in our studied system. This is the first time to use magnetic mode to enhance surface enhanced Raman spectroscopy, and it will promote the applications of magnetic modes in surface enhanced spectroscopy.

5. Studies on acoustic plasmon mode properties. In infrared and THz frequencies, graphene plasmons have shown great applications in surface enhanced spectroscopy, optical modulator and sensing because of their ultra-confined and enhanced field, highly tunable by electric gating. Herein, we studied the novel plasmonics properties of graphene resonator-gold substrate. Graphene acoustic modes with