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博 士 学 位 论 文

基于壳层隔绝模式的等离激元增强光谱

Plasmon-enhanced spectroscopy with shell-isolated mode

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摘 要

当可见光照射在具有纳米结构的贵金属（金、银、铜）表面时，或者波矢量与介质-金属界面的波矢匹配时，会引起金属内部电子的群体性振荡——等离激元共振（plasmon resonance）。因为等离激元共振的激发，金属纳米结构会将可见光光子局限在亚波长范围的近场里。同时，随之被增强的局域电磁场会使表面附近探针分子的拉曼或荧光信号放大，该现象被称为表面增强拉曼光谱（SERS）或荧光光谱（SEF）。表面增强拉曼光谱是一种基于表面等离激元共振的纳米光子学技术，因为能够提供类似于“指纹”一样的特征振动光谱信息，而在材料科学、表面科学、生命科学以及人们实际生活中备受关注。尤其是当两个纳米结构互相靠近时，因为等离激元的耦合，纳米间隙中的局域电磁场会进一步增强并形成“热点”。在这些“热点”中，可以实现单分子水平的拉曼光谱检测和化学成像。然而，SERS仍然存在两个限制因素，第一是基底材料的选择局限在金、银、铜等类自由电子材料中，第二是需要具有纳米级粗糙的基底形貌才能提供表面等离激元增强活性。2010年，我们课题组发明了壳层隔绝纳米粒子增强拉曼光谱技术（SHINERS），可以适用于任意材料的表面和任意形貌的基底，突破了对基底材料和形貌的局限。然而，SHINERS技术依然存在着一些局限，比如原先使用金纳米粒子作为内核时无法应用于绿光波段以下激发光，纳米粒子体系的空间分辨率受限于光斑尺寸等等。因此，本论文针对这些限制因素，从改进壳层隔绝纳米粒子（SHINs）的合成方法学开始，进一步优化SHINERS技术中的耦合模式，提高SPR增强能力，最终实现单分子光谱检测以及埃级别空间分辨率的电磁场分布表征。本论文的主要内容如下所述。

1. 因为金纳米材料在~530 nm的带间跃迁，令以金纳米粒子为内核的SHINERS技术受限于该波段以下激发光的应用。而银纳米结构则是理想的替代品，但是银因为其高化学活性，容易在表面形成氧化物或硫化物薄膜，并在溶液相中析出银离子，这也令银壳层隔绝纳米粒子（SHINs）的合成变得困难。我们使用硼氢化钠水溶液对银溶胶进行前处理，消除了银离子和表面氧化物的影响，成功制得了壳层致密、极薄的Ag SHINs。Ag SHINs抗化学腐蚀性强，同时还具有很好的稳定性，即使存放16个月后，其SHINERS活性衰减不超过20%，因此它在实际应用以及商品化中具有巨

大潜力。为了突破空间分辨率的限制，我们同时制备壳层隔绝银针尖，并适用于壳层隔绝针尖增强拉曼光谱实验中（SITERS）。正因为极薄、致密壳层的存在，我们还将Ag SHINERS和SITERS技术成功地应用于表面等离激元调控化学反应过程中。

2. 在以往文献报道中，纳米粒子增强荧光倍数一般仅有10~20倍左右。为了进一步提高表面增强荧光的分析灵敏度，我们使用金属膜-隔绝层-荧光分子层-Ag SHINs耦合结构，加速了有机荧光团的自发辐射过程并提高量子效率。在纳米腔中，局域态密度在表面等离激元共振频率下被放大，进而使荧光分子的辐射跃迁过程成为主要衰减渠道。同时，Ag SHINs作为纳米天线，使荧光光子与纳米粒子的散射发生耦合，辐射波瓣的改变令收集效率进一步被提高。综合上述过程，我们使用Ag SHINs调控荧光辐射过程，使荧光信号被增强了5个数量级。在此耦合结构中，被增强的局域场荧光信号有利于单分子的发射谱，我们还同时获得了单分子的共振拉曼光谱。

3. 等离激元纳米腔的新奇现象来自于物理场在亚波长范围下的空间局域。当这个空间局域分解为垂直方向和横截面内时，实验以及理论研究皆表明横截面内的空间局域可以达到纳米量级，这是超高空间分辨率光谱成像和化学识别的基础。但是对垂直方向上的等离激元局域分布，知之甚少，无法探知固定纳米间隙中的电磁场分布。我们利用一系列HS-nV16-nH型viologen分子，总链长一致，但是4，4’-联吡啶基团在垂直方向上可以~2.1 Å的分辨率调节。Viologen分子在原子级平滑的金单晶表面进行高度有序的自组装后，与Au SHINs粒子共同构筑间距固定不变的纳米间隙。以4，4’-联吡啶基团的拉曼光谱强度分布，发现电磁场增强因子最强点出现在靠近Au SHIN一端，整体趋势与理论计算结果相符，实现了对固定纳米间隙中，具有埃级别空间分辨率的电磁场分布表征。

关键词：等离激元共振；壳层隔绝纳米粒子增强光谱；壳层隔绝针尖增强光谱；电化学拉曼；单分子光谱；埃级别空间分辨率

Abstract

When a noble metal nanostrucutre surface is illuminated by a visble light, or the light meets the wave vector at a dielectric-metal interface, a collective oscilation of electrons within noble metal (e.g. Au, Ag, and Cu) will be induced, which is known as plasmon resonance. Due to the excitation of SPR, photons will be confined in a sub-wavelength near field. Meanwhile, Raman scattering or fluorescence singals of probes nearby will be manified by the enhanced local electromagnetic field. These are surface-enhanced Raman scattering (SERS) and fluorescene (SEF), respectively. SERS is a SPR-based nanophotonic technique and could provide ultrasensitive “fingerprint” vibrational information. It have greatly expanded our knowledge in surface science, material science, life science and people’s daily life. Especially, the local electromagnetic field would be significantly enhanced due to the coupling effect in a nanogap resulted from two apporaching nanostructures. The “hot” spots have been used for single-molecule Raman scattering and chemical image. However, there are two main limitations of SERS for the applications, concerning a morphology-specific property and a poor material generality. In 2010, our group invented a new approach called shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS). It has overcome the long-term drawbacks in SERS and could be applied on atomically flat surface without the material-speicific limitation. However, there are several aspects of SHINERS need to be improved, such as an ideal candidate of SHINERS core for application in the wavelength below ~530 nm (the plasmonic perfomance of Au nanoparticle in this range is poor due to the interband transition), and a higher spatial resolution. Hence, the primary content of the research in this thesis is summarized as following:

1. Ag nanomaterial is an ideal candidate for SHINERS core due to the high quality factor across the spectrum from ~300 to 1200 nm wavelength. However,

the surface of Ag is easily oxidized or sulfurized in an ambient condition. In addition, Ag+ ion release will significantly hamper the shell coating in SHINERS synthesis. Herein, we used a simple treatment of Ag sol with NaBH4 solution to avoid the formation of silver oxide or sulfide on the Ag surface. The as-prepared Ag SHINs exhibited excellent plasmonic capability with remarkable chemical stability even after a storage around 16 months. Ag SHINs are highly suitable for practical applications and the potential commercialization. Meanwhile, to further improve the spatial resolution, we also invented shell-isolated tip-enhanced Raman spectroscopy (SITERS) for near-field optical technique. Both of Ag SHINERS and SITERS methods feature an alternative photocatalysis reaction pathway by blocking “hot” electrons.

2. Normally, the enhancement is only about 10~20 fold in the previous publications. To further enhance the sensitivity in SEF, we have employed a Ag film-spacer-fluorophore-Ag SHINs coupling configuration to accelerate spontaneous emission process of organic fluorophore and improve quantum yield. The local density of states is maximized around the SPR range in the nanocavity which greatly enhanced the radiative decay rate. Meanwhile, with the presence of plasmonic nanoatenna, the fluorescence photons could be coupled with the directional plasmon scattering pattern, which increses the collection efficiency. As result, a emission enhancement more than 105 fold was achieved. With this coupling mode, single-molecule Raman scattering along with single-molecule fluorescence signal is obtained at room temperature.

3. Previous investigations of “hot” spot are based on a coupling configuration with various nanogaps. However, it is quite difficult to probe the electromagnetic field distribution in the “hot” spot. A set of viologen-tye self-assembly monolayers have been used as fixed nanogaps between Au(111) surface and Au SHINs, where the 4,4’-bipyridine moiety could be shifted along the vertical direction with ~2.1 Å spatial resolution. Therefore, the electromagnetic field in the fixed

nanogap could be obtained from Raman scattering intensity of 4,4’-bipyridine moiety. As result, the highest electromagnetic field enhancement is observed towards Au SHIN within the nanogap, and the tendency of electromagnetic field distribution correlates well with the FDTD simulation.

Keywords: Plasmon resonance; shell-isolated nanoparticle-enhanced spectroscopy (SHINES); shell-isolated tip-enhanced spectroscopy (SITERS); electrochemical Raman (EC-Raman); single-molecule spectroscopy (SMS); angstrom scale spatial resolution

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