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硕士学位论文

基于银纳米粒子发展面向实际应用的高稳定和高灵敏的表面增强拉曼光谱增强基底

Ag NPs-based SERS substrates with high stability and sensitivity for practical applications

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摘 要

表面增强拉曼光谱（surface enhanced Raman spectroscopy，SERS）因具有单分子水平的高灵敏度，指纹图谱的高能量分辨率，衍射极限的空间分辨率和水环境友好等特点，在表面科学、分析科学和生物医学等方面获得了广泛的应用。随着便携式拉曼光谱仪器的问世，SERS在食品安全、环境监测、国防和公共安全等领域的应用前景也越发为研究者所关注。然而，迄今为止，SERS技术通常仅局限于这些领域的实验室基础研究，对于在实际体系中的应用还存在着许多问题。特别是如何获得高灵敏、高稳定、高重现性和易商品化的SERS基底，已成为SERS领域的热点和重点之一，是SERS面向实际应用的基石和瓶颈。

因此，本论文致力于高重现、高稳定和高灵敏SERS基底的开发及其应用。具体工作如下：

（1）高重现性、高稳定性和高灵敏SERS基底的开发。实现复杂体系中痕量物种的检测是分析科学的核心问题之一，也是SERS应用的重点。虽然，化学法制备的SERS基底实现了对具有共振拉曼效应的分子的单分子水平的检测，但是，制备时引入的保护剂往往会干扰痕量目标物种的检测，而保护剂的存在又是SERS基底稳定性的一个重要保证。因此，围绕如何保证SERS基底的稳定性的同时提高其灵敏度这一科学问题，本文开发了一种高稳定性和高灵敏度的Ag纳米基底，在合成方法上摒弃了传统柠檬酸钠还原法，选用盐酸羟胺和硼氢化钠双还原剂共同作用制备了Ag纳米基底。通过性能比对发现，本方法获得的SERS基底在保证一定稳定性和重现性的同时，其灵敏度相对于柠檬酸钠法提高了一个数量级。

（2）发展面向实际应用的SERS检测方法。将高稳定性和高灵敏度SERS基底用于化学战剂模拟剂DMMP的检测，通过改变SERS基底的预处理条件，发现SERS基底处于半干半湿状态时可测得很好的DMMP拉曼信号，但这种方法要求苛刻，无法满足单兵作战实际操作需求。因此，基于预团聚方法，本文开发了一种新型固态基底，实现了DMMP的实时、快速、便捷检测。

（3）金属硫化物核壳结构纳米粒子合成及应用研究。本研究包括三方面的内容，首先是发展了一种Au@SiO2纳米粒子的针孔填补技术；其次研究了碱性甲醇氧化

中间体CO在Au@Au2S/Pt电极上的吸附行为；再次制备了Ag@Ag2S纳米粒子，并探讨了其在甲基橙和罗丹明B的光催化降解反应中的应用。

关键词：SERS；高灵敏；高稳定；DMMP；超薄壳层

Abstract

Surface enhanced Raman spectroscopy has a wide application in fields such as surface science, analytical science and biomedicine for its high sensitivity up to single molecule level, high-energy resolution of fingerprint spectra, spatial resolution nearing diffraction limit and little interference from water and so on. With the advent of portable Raman spectrometer, SERS has attracted much attention in research areas of food safety, environmental monitoring, national defense and public security and other areas. However, SERS has been limited to fundamental laboratory studies at present. There still exist many problems for its applications in practical systems. In particular, it has been a hot and key issue in the SERS field to obtain SERS substrates, with high sensitivity, stability, reproducibility and easy commercialization. This is aslo the foundation stone as well as bottleneck for practical applications. Hence, this thesis is mainly devoted to preparing SERS substrates with high reproducibility, stability and sensitivity, and their applications. Specific works are as follows:

(1) Development of highly reproduce, stable and sensitive SERS substrates. Trace species detection in complex system is one of the core problems in analytical science, and is aslo a key point in the application of SERS. Although, SERS substrates prepared with chemical methods can achieve single molecule detection of molecules with resonance raman effect, the protective agents introduced in preparation process, which can ensure the stability of the SERS substrates, often interfere with the detection of trace amounts of target species. To this end, this thesis developed a new Ag NPs substrates with high stability and sensitivity. This method abandoned the traditional practice of using sodium citrate as the reducing agent, instead, hydroxylamine hydrochloride and sodium borohydride were chosen to synthesize the Ag NPs. By comparison, we found that not only the SERS substrates obtained with this method can achieve

desirable stability and reproducibility, but aslo their SERS sensitivity is one order of higher than those prepared with the sodium citrate method.

(2) Developing SERS detection methods for practical applications. The highly stable and sensitive SERS substrates were used to detect the DMMP molecule, which is a chemical warfare agent simulant. By changing the pretreatment conditions, it was found that good Raman signals of DMMP could be detected, when the SERS substrates are in the metastable state. However, this approach is demanding in erpertise and unable to be operated by non-professionals. This thesis developed a novel kind of solid substrates based on pre-aggregating, thus enabling real-time, fast, and convenient detection.

(3) The synthesis and application of metal sulfide core-shell structure nanoparticals. This studies inculed three parts. Firstly, developing an technology to filling of the pinhole in Au@SiO2; Secondly, the adsorption behavior of alkaline methanol oxidation intermediates CO absorded on Au@Au2S/Pt electrode were studied. Thirdly, Ag@Ag2S nanoparticles were fabricated and applicated in photocatalytic degradation of methyl orange and Rhodamine B.

Keywords: SERShigh sensitivityhigh stabilityDMMPultrathin-shell

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