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工 学 博 士 学 位 论 文

激光制备石墨烯/银复合结构 SERS 器件及应用研究

Laser Fabrication of Hybrid Graphene/Silver SERS Chips and Their Applications

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摘 要

石墨烯/银复合结构 SERS 器件可充分发挥石墨烯与银纳米结构的特性，具有良好的性能。银纳米结构 SERS 活性强，但稳定性差，在空气中易氧化，限制了银 SERS 器件的应用。石墨烯具有原子级的厚度，良好的光学透过率，稳定的化学性质，是 SERS 器件理想的壳层材料，可有效阻止银纳米结构与探针分子及周围环境接触，提高基底稳定性。并且石墨烯本身还具有拉曼信号增强、荧光猝灭、探针分子富集等功能，使石墨烯/银复合结构成为 SERS 信号检测的理想平台。论文针对石墨烯/银复合结构 SERS 器件制备方面存在的问题展开研究工作，提出了两种工艺简单的石墨烯/银复合结构 SERS 器件快速制备方法，并根据 SERS 器件的特性，研制了便携式、低成本的拉曼光谱检测样机。论文的主要研究工作以及成果如下：

（1）根据 L-CVD 制备石墨烯的原理，研制了一套可对制备参数进行精密监测与控制的石墨烯快速制备装置，并通过实验研究了腔压、激光功率密度及激光扫描速度对石墨烯生长的影响，实现了高质量多层石墨烯的快速制备。

（2）提出一种基于脉冲激光原位沉积快速制备大面积银纳米结构的方法，并基于该方法制备了 G/Ag/LTSi 复合结构 SERS 器件。G/Ag/LTSi 的拉曼增强因子为 2.6×10^{7}，并且性能稳定，在空气中放置 50 天，仍能保持良好的 SERS 活性。

（3）提出一种使用飞秒激光快速制备表面带有绒毛状纳米结构的银纳米光栅阵列的方法，并基于该方法制备了 G/Ag_LIPSS/Si 复合结构 SERS 器件。G/Ag_LIPSS/Si 的拉曼增强因子为 3.4×10^{6}，稳定性好，并且器件表面各区域 SERS 信号强度的相对标准偏差<2.5%，具有较好的信号一致性，可用于定量/半定量拉曼检测的场合。

（4）根据石墨烯/银复合结构 SERS 器件的特性，初步研制了成本低、体积小、光路简单的便携式拉曼样机。拉曼样机与 G/Ag/LTSi、G/Ag_LIPSS/Si 复合结构 SERS 器件配合使用，对探针分子溶液的最低检出限分别为 10^{-9}mol/L 与 10^{-8}mol/L，实现了痕量物质的检测。并且开展了初步的应用研究，使用拉曼样机与复合结构 SERS 器件分别对乳制品中是否添加三聚氰胺进行快速筛查以及对尿

液中尿酸浓度是否超标进行快速检测。

论文使用激光技术实现了石墨烯/银复合结构 SERS 器件的快速制备，拓展了激光技术在 SERS 器件制备中的应用。论文制备的石墨烯/银复合结构 SERS 器件与便携式拉曼样机配合使用可对痕量物质进行有效检测，在食品安全、环境监测、疾病诊断等领域具有良好的应用前景。

关键词：表面增强拉曼散射 激光加工 石墨烯快速制备 石墨烯/银复合结构

Abstract

Graphene/silver is a promising composite structure for SERS chips with both the excellent performance of graphene and silver nanostructures. Graphene has been envisioned as one of the best shell materials for SERS chips to improve the stability owing to its atomic thickness, excellent optical transmittance and stable chemical property. Moreover, graphene can also function as additional signal enhancer, fluorescence quencher, and molecule enricher for SERS applications, making graphene/silver hybrids become an excellent platform for SERS detection.

In this thesis, two approaches with low cost and fast speed based on laser processing for fabricating graphene/silver hybrids were proposed, in order to solve the issues in preparation of graphene/silver hybrid SERS chips. Furthermore, a portable and low-cost prototype for detecting SERS signals on the graphene/silver hybrid SERS chips was developed. The main work and results of this thesis are summarized as follows:

(1) An automatic setup based on the laser-assisted chemical vapor deposition method was developed for the rapid synthesis of graphene. All the fabrication parameters that affect the quality and number of graphene layers, such as laser power, laser spot size, laser scanning speed, pressure of vacuum chamber, and flow rates of gases, can be precisely controlled and monitored by this setup during the preparation of graphene. The experimental results showed that multilayer graphene with few defects can be synthesized rapidly by this setup.

(2) An approach based on the pulsed laser insitu deposition was put forward to prepare large-area silver nanostructures. The graphene/silver SERS chip with the hybrid structures of graphene/silver film/laser-textured Si surface (G/Ag/LTSi) was obtained after graphene was transferred to the surface of silver nanostructures. The G/Ag/LTSi SERS chip achieved an enhancement factor of 2.6×10^7 and exhibited a stable performance. Its excellent SERS activity can be maintained for 50 days in air at least.

(3) A method based on femtosecond laser induced periodic surface structures was proposed for the rapid preparation of large-area silver nano-grating arrays with fluffy nanostructures. After the graphene was transferred to the surface of silver nano-grating arrays, the graphene/silver SERS chip (G/Ag_LIPSS/Si) with periodic silver nano-

structure was obtained. The enhancement factor of G/Ag_LIPSS/Si was 3.4×10^6. Moreover, the G/Ag_LIPSS/Si exhibit good stability and homogeneity to boost the Raman intensity. The relative standard deviation of SERS intensity from different areas of G/Ag_LIPSS/Si was less than 2.5%, which suggested that G/Ag_LIPSS/Si can be used for quantitative or semi-quantitative Raman detection.

(4) According to the features of fabricated graphene/silver hybrid SERS chips, a portable and low-cost prototype with simple optical configuration for the detection of SERS signals was developed. The detection limits achieved by this Raman prototype with the Raman enhancement of G/Ag/LTS and G/Ag_LIPSS/Si SERS chips were 10^{-9}mol/L and 10^{-8}mol/L, respectively. Furthermore, the Raman prototype with the signals enhancement of hybrid graphene/silver SERS chips were utilized to detect whether to add melamine in milk and whether the uric acid concentration was exceeded, respectively.

In this thesis, new technologies based on laser processing were exploited for the rapid fabrication of hybrid graphene/silver SERS chips. In addition, a portable Raman prototype was developed according to the features of fabricated SERS chips. With the Raman signal enhancement of graphene/silver SERS chips, the Raman prototype can realize the detection of trace substances with low cost and fast speed, which is a powerful tool for food testing, disease diagnosis and environmental monitoring.

Keywords: Surface-enhanced Raman scattering; Laser processing; Fast growth of graphene; Graphene/silver hybrids

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