

A study on synthesis and assembly of metallic nanostructures for plasmonic gas sensors

郭, 昊

<https://hdl.handle.net/2324/7363831>

出版情報 : Kyushu University, 2024, 博士 (工学) , 課程博士
バージョン :
権利関係 :



氏 名 : 郭 昊

論 文 名 : A study on synthesis and assembly of metallic nanostructures for plasmonic gas sensors

(プラズモニックガスセンサー向けの金属ナノ構造の合成および構築に関する研究)

区 分 : 甲

論 文 内 容 の 要 旨

Optical sensing technology has found extensive applications across multiple fields owing to its ultrahigh sensitivity, real-time response characteristics, and non-destructive detection advantages. Surface Plasmon Resonance (SPR), serving as an effective tool for investigating optical properties of nanomaterials and biomaterials, achieves ultrasensitive detection of molecular surface changes through resonant coupling between incident light and free electrons on metallic surfaces. This unique detection mechanism has driven its innovative applications in food safety, drug screening, environmental monitoring, and medical diagnostics. While Localized Surface Plasmon Resonance (LSPR) and Surface-Enhanced Raman Scattering (SERS) technologies based on the plasmonic sensors have achieved major breakthroughs in biomacromolecule detection, traditional applications have primarily been confined to macromolecular systems, with efficient detection of small molecules such as gases remaining a significant challenge. The optimization of sensor performance mainly relies on rational design of plasmonic nanostructures and precise control of their surface properties. Through careful engineering of material composition and nanoscale architecture, significant improvements in detection sensitivity and response characteristics can be achieved. This research focuses on enhancing nano plasmonic-based gas sensing performance through material design and fabrication methods. The thesis comprises five chapters, with the main contents as follows:

Chapter 1 provides a comprehensive overview of the research background. It systematically introduces various gas sensing technologies, with particular emphasis on the fundamental detection principles, current detection strategies, and state-of-the-art fabrication methods of plasmonic nanosensors. The chapter also presents a comparative analysis of different sensing technologies, highlighting their respective advantages and limitations.

Chapter 2 explores bimetallic nanoparticles, which exhibit unique physicochemical properties and surface characteristics due to the synergistic interactions between the electronic states of two metals. These properties differ significantly from their monometallic counterparts. Among these nanostructures, Au/Ag core-shell architectures have attracted considerable attention due to their distinctive surface plasmon resonance properties, superior catalytic activity, and potential applications in sensing. This chapter introduces a novel fabrication approach for plasmonic nanosensors based on Au@Ag core-shell nanoarchitectures. The synthesis protocol begins with the controlled preparation of Au nanoseeds on glass substrates through thermal dewetting. Subsequently, plasmon-enhanced photochemical deposition of Ag shells is performed. Under

visible light irradiation, the localized surface plasmon resonance of Au nanoseeds generates enhanced electromagnetic fields. These fields direct the selective reduction of silver ions, enabling precise control over the formation of uniform Ag shells.

Chapter 3 addresses the critical challenge of gas molecule adsorption capability in sensor performance. Building upon our previous work on Au@Ag core-shell nanostructures, we recognize that noble metal nanostructures inherently lack enrichment capabilities for gas molecules, limiting LSPR-based gas sensing effectiveness. To overcome this limitation, we utilize ZIF-8, a representative metal-organic framework that exhibits superior performance in gas adsorption and storage due to its porous structure. This chapter presents the development of an enhanced LSPR gas sensor using gold nano-urchin nanoparticles as the LSPR basement substrate, encapsulated with MOF nanoparticles in a core-shell structure. The incorporation of ZIF-8 significantly enhances the gas response sensitivity of the LSPR sensor, increasing detection signals for various gases by 5 to 7 times. Furthermore, the sensor demonstrates effective responses to previously undetectable gases, such as ammonia. To enhance selectivity, a layer of PEDOT: PSS film is spin-coated onto the LSPR sensor. As a specific material for ammonia detection, the chemical interaction between PEDOT: PSS and ammonia further improves the sensor's detection capabilities, showing superior performance compared to other gases.

Chapter 4 presents the development of a novel plasmonic gas sensor optimized for SERS-based gas detection applications. While Chapters 2 and 3 demonstrated enhanced plasmonic sensor gas response through in-situ growth strategies using LSPR detection methodology, SERS emerges as a powerful complementary technique for molecular identification due to its unique fingerprint characteristics. This chapter details a scalable fabrication strategy for plasmonic nanosensors utilizing interfacial self-assembly. The approach begins with the synthesis of monodisperse silver nanoparticles with precisely controlled dimensions. These nanoparticles are subsequently assembled into densely packed monolayers through a sophisticated Marangoni effect-driven oil/water/oil (O/W/O) tri-phase interfacial system. The interfacial tension gradient directs the controlled migration and assembly of silver nanoparticles, while the addition of $\text{TBA}^+\text{NO}_3^-$ effectively reduces the Coulomb forces between nanoparticles due to charge effects, enabling more compact nanoparticle arrays. Subsequently, by integrating the fabricated sensors with Surface-Enhanced Raman Scattering (SERS) detection technology, we achieved partial visualization of gases.

Chapter 5 presents a comprehensive summary of the experimental results and provides critical insights into future research directions. The chapter discusses potential improvements in sensor design, and detection methodologies for advancing the field of plasmonic gas sensing.