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Recent Advances in Lithographic-Free Fabrication and Utilization of Well-Ordered AuNP LSPR Sensors

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Summary:

This study presents a comprehensive fabrication technology for LSPR sensors to address critical challenges, including high cost and low sensitivity. The fabrication process involves two key steps: the self-ordering growth of porous anodic alumina (PAA) and the template-assisted dewetting of thin gold film, resulting in a well-ordered AuNP layer. This work focuses on achieving large-scale ordering without lithography processes, improving the shape control of AuNPs, and exploring their utilization as gas sensors.

Keywords: Localized Surface Plasmon Resonance, Gold Nanoparticles, Porous Anodic Alumina, Thin-Film Dewetting, Well-Ordered Nanoparticle Layer

Background, Motivation and Objective

Numerous existing biosensing methods utilized in healthcare and environmental monitoring are characterized by their time-consuming nature, high costs, bulkiness, and the need for skilled personnel and well-equipped laboratories. Consequently, crucial services like disease diagnostics and monitoring water or air quality often suffer neglect due to economic constraints, leading to millions of casualties annually. Hence, significant research efforts are currently directed towards reducing costs, aiming to yield substantial improvements in global health [1].

In recent decades, localized surface plasmon resonance (LSPR) has gained significant scientific attention owing to its simplicity in multiplexing, high sensitivity, real-time analysis, and label-free detection, all while remaining cost-effective. Yet, a considerable setback lies in the expensive fabrication of nanostructured plasmonic sensors.

Our previous studies have showcased the lithographic-free fabrication of well-ordered layers of gold nanoparticles (AuNPs). This synthesis method relies on a template-assisted solid-state dewetting process of thin gold films on hexagonally ordered aluminum templates formed via porous anodizing, as illustrated in Fig. 1. Subsequently, these layers were transferred onto a transparent glass substrate to serve as effective LSPR sensors.

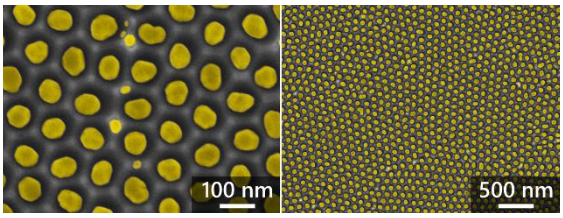

Fig. 1. SEM images of AuNPs on an aluminum template (false colors).

We demonstrated the biosensing performance of these sensors for DNA detection [2] and effective signal amplification for surface-enhanced Raman spectroscopy [3].

Description of the New Method or System

This work explores a novel approach to porous anodizing characterized by gradual progression. As shown in Fig. 1, conventional anodizing under standard conditions results in ordered domains. The domain misalignment is caused by spontaneous pore nucleation, which co-occurs over the whole surface at the beginning of the anodizing process. Therefore, while technically challenging, gradual anodizing holds promise for achieving single-domain self-ordering across a sizable area.

Moreover, we provide a brief demonstration of an additional method for modifying the shape of dewetted AuNPs by leveraging the surface energy of the interfacial layer, as predicted from the Young–Dupré model describing the contact angle.

Lastly, we present a new application of our LSPR sensors in room temperature gas sensing [4]. This topic is related to the abstract “Benchmarking the Gas Sensitivity of LSPR Sensors with a New Parameter” by Attila Bonyár.

Results

AuNPs’ shape and size can be tuned by several parameters, such as the thickness of the thin deposited gold film, dewetting temperature, etc. [2]. We demonstrate that surface contamination and oxidation are crucial in the AuNP shape.

Carbon contamination is a common issue. Its rate depends on the storage conditions and time. Fig. 2 illustrates the difference between gold (8 nm) dewetting over a pristine Al template and a template with 4 nm of flashed carbon layer.

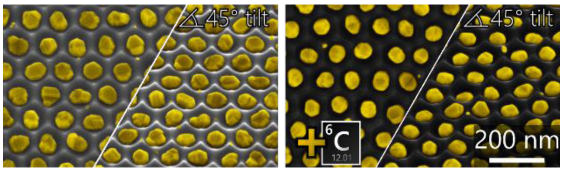

Fig. 2. SEM images of AuNPs on an aluminum template without (left) and with 4 nm carbon layer (false colors).

A similar effect is observed with aluminum oxidation. In ambient conditions, the native oxide layer can grow to a thickness ranging from 4 to 10 nm. This oxidation also smoothens the template edges causing undesirable dewetting outcomes (e.g., uneven splitting and AuNP merging).

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