

Fabrication of Flexible Plasmonic Nanoparticle Arrays with Sub-Wavelength Period Using Aluminum Sacrificial Layer and AAO Template Transfer

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Abstract

Dynamic and tunable flexible plasmonic structures offer significant advantages in functional applications across various fields such as biosensing, photodetection, nonlinear optical devices, and quantum information processing, due to their multifunctionality, reversibility, and adaptability to complex environments. Among these, PDMS (polydimethylsiloxane), as a transparent and flexible substrate, is widely used. However, PDMS is a non-polar material with low surface energy, making it difficult for metal particles to adhere effectively. In practical applications, metal particles may detach due to stress concentration, leading to instability of the deposited metal particles over time. Here, we propose a method using an aluminum sacrificial layer anodized aluminum oxide (AAO) template transfer technique to fabricate flexible plasmonic nanoparticle arrays with subwavelength periodicity. This work designs more practical plasmonic nanostructures, providing a new pathway for dynamically tunable plasmonic systems.

Keywords

Plasmonic Nanostructure; Localized Surface Plasmon Resonance; Dynamic Tunability.

1. Introduction

Surface plasmon resonance (SPR) refers to the collective oscillation of free electrons in metal nanostructures induced by light at a specific resonance wavelength. SPR has attracted widespread attention due to its potential to bypass the conventional optical diffraction limit and enhance light-matter interactions.[1, 2] In recent years, significant efforts have been devoted to enhancing the functionality of plasmonic devices by achieving dynamic tunability. For example, Asad Nauman proposed a plasmonic mechanical sensor capable of distinguishing strain direction and magnitude.[3] Chen Zhang introduced a polarization-insensitive, stretchable TiO₂ metasurface.[4] Hsiang-Ting Lin presented a reliable method for tuning circular dichroism spectra by stretching the device.[5] On the surfaces of these devices, metal particles typically adhere to PDMS through van der Waals forces rather than chemical bonding. However, the physical adhesion is weak, and metal particles are prone to detachment or abrasion due to external forces, friction, or other environmental factors. To enhance the adhesion of metal particles, surface treatments such as oxygen plasma treatment, UV exposure, or the introduction of functional groups are commonly employed. Despite these surface modification methods, the adhesion of metal particles remains weak, leading to detachment issues. Therefore, achieving a practical solution remains a challenge.

In this work, we propose a method using an aluminum sacrificial layer and anodized aluminum oxide (AAO) template for transferring flexible plasmonic nanoparticle arrays with sub-wavelength periodicity. The method involves creating the plasmonic array on an AAO template, followed by transferring and embedding the array into a PDMS film using aluminum as the sacrificial layer.

Compared to traditional methods, this method significantly enhances the adhesion of metal particles. Additionally, the high-precision pore structure of the AAO template ensures a uniform distribution and tunability of the transferred nanoparticle arrays, which is crucial for surface plasmon applications. The flexible plasmonic nanoparticle arrays produced by this method not only offer significant advantages in enhancing light-matter interactions but also effectively resist environmental influences, improving device stability and durability. This technique holds broad application prospects in flexible electronics, sensors, and optoelectronic devices.

2. Results

2.1 Design and Performance of Dynamic, Tunable Flexible Plasmonic Films

The theory of localized surface plasmon resonance (LSPR) suggests that resonance enhancement can occur through the structure of plasmonic nanoparticle arrays when interacting with a specific incident wave. To fabricate plasmonic arrays, we utilize the AAO template method to obtain metal nanoparticles. This method offers advantages such as low manufacturing cost and large array coverage, making it well-suited for large-scale production. Additionally, to ensure that metal particles on PDMS are less likely to be removed, we designed the metal particles to be embedded within the PDMS surface (Fig. 1a). The plasmonic array structure consists of silver hemispherical particles arranged in a hexagonal lattice, consistent with the array formation generated by the AAO template method.

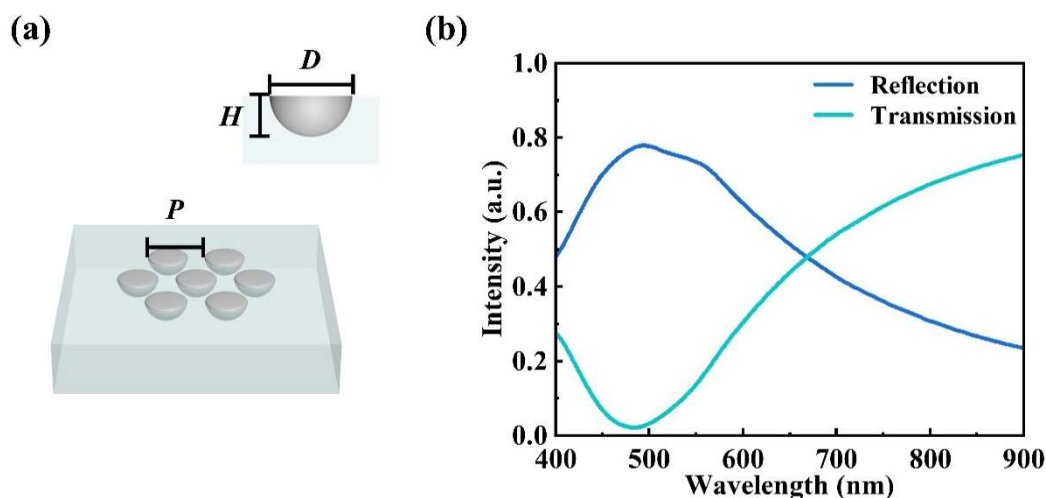


Fig. 1 Schematic of plasmonic structure and its simulated spectrum

As the source of the localized surface plasmon resonance modes, the silver hemispheres on the flexible PDMS substrate can easily tune the LSPR peak by adjusting structural parameters such as hemisphere height (H) and diameter (D). Furthermore, compared to individual particles, the near-field coupling between particles in the array significantly influences the plasmonic resonance characteristics, leading to shifts in the resonance peak. Through finite-difference time-domain (FDTD) simulations, we calculated the reflection and transmission spectra when $H = 40$ nm, $D = 80$ nm, and $P = 110$ nm (Fig. 1b).

2.2 Fabrication and Characterization of Dynamic, Tunable Flexible Plasmonic Films

The first step in the fabrication process is the preparation of the AAO template. A mixed solution of HClO_4 and $\text{C}_2\text{H}_5\text{OH}$ in a 1:3 volume ratio was used to electropolish a pure aluminum sheet (99.999%). The polished aluminum sheet was then placed as the anode, with a current of 1.2 A and the temperature controlled at 0°C . The first anodization was carried out in 0.3 M oxalic acid at a constant voltage of 45 V, with the temperature maintained at approximately 4°C , for 3 hours, forming

the first layer of the AAO template. Subsequently, the first AAO template was removed by etching in a mixture of 6 wt% phosphoric acid and 1.8 wt% chromic acid at 60°C. The anodization was repeated for 180 seconds under the same conditions as the first anodization, resulting in a regular AAO template with an initial pore diameter (D) of 40 nm and period (P) of 110 nm. Finally, the AAO template was further etched using phosphoric acid, and by adjusting the etching time, we were able to control the pore diameter and distance, with the relationship between D and etching time (t_e) given as follows.

$$D = 40 + 1.4 t_e \quad (1)$$

Next, the AAO template was transferred to a silicon substrate coated with 100 nm of aluminum using a wet transfer process. A protective layer was formed by spin-coating a photoresist (AZ1505) and a 30 wt% PMMA solution onto the sample, followed by curing. The protective layer only needs to fully cover the AAO and does not require a specific thickness. The sample was then immersed in a CuSO_4 solution (0.88 mol/L) until the aluminum base was completely dissolved. Afterward, the protected AAO template was placed in 6.14 wt% phosphoric acid at 30°C for 30 minutes to remove the bottom blocking layer of the AAO template, resulting in a protective layer-AAO composite film. The final step involved transferring the protective layer-AAO composite film to the aluminum-coated silicon substrate and dissolving the photoresist and PMMA with acetone.

The fabrication of the dynamic, tunable flexible plasmonic structure is illustrated in Fig. 2. First, silver was deposited onto the AAO template by electron beam evaporation. The AAO template was then removed with adhesive tape to obtain the plasmonic array. After degassing, PDMS was directly poured onto the sample and cured at 80°C for 15 minutes. The cured sample was then placed in a NaOH solution to etch the Al layer, transferring the silver nanoparticle array onto the PDMS substrate, resulting in a dynamic, tunable flexible plasmonic film.

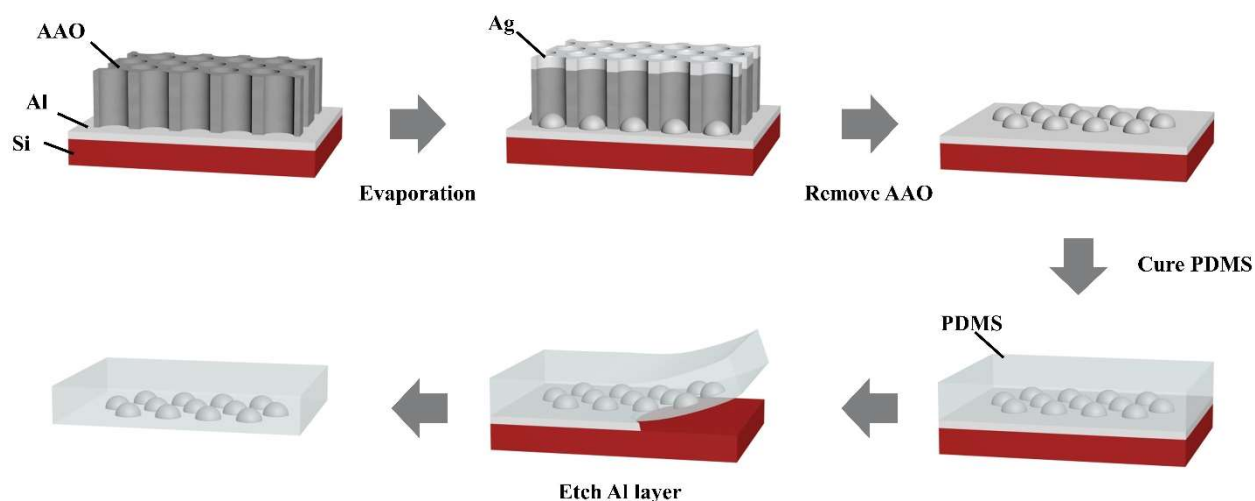


Fig. 2 The fabrication of the dynamic, tunable flexible plasmonic film

The flexible plasmonic film is shown in Fig. 3a. Experimental results showed that the dynamic, tunable resonator structure exhibited high reflectivity and superior performance of the plasmonic resonance modes (Fig. 3b), which is consistent with the results from FDTD simulations.

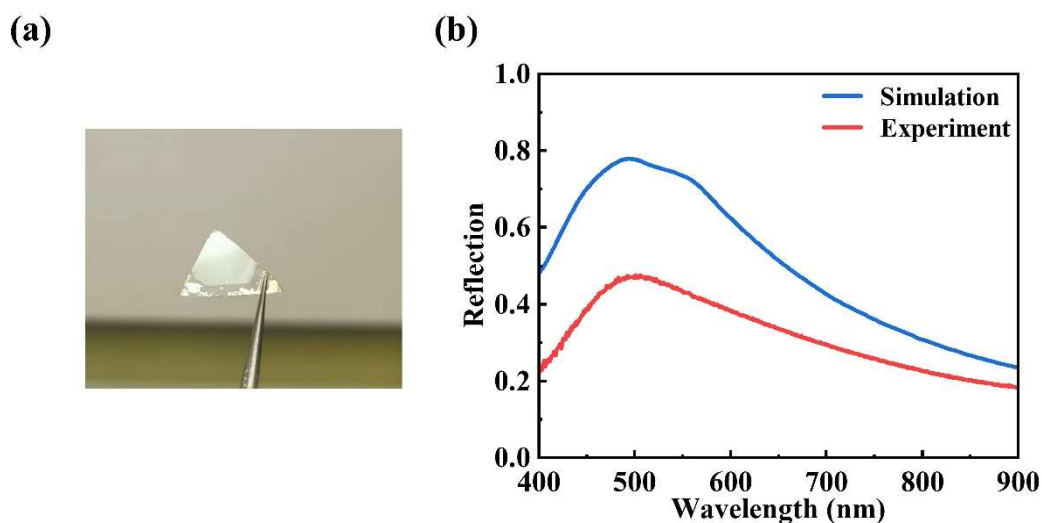


Fig. 3 Flexible plasmonic film samples and reflection spectra

3. Conclusion

In this work, we presented a novel approach for fabricating dynamic, tunable flexible plasmonic films using an AAO template and an aluminum sacrificial layer. The method involves the creation of a plasmonic nanoparticle array on the AAO template, followed by the transfer and embedding of the array into a PDMS substrate, which significantly enhances the adhesion of metal particles compared to conventional methods. The resulting plasmonic arrays, with their precise tunability through parameters such as nanoparticle height, diameter, and array period, offer enhanced localized surface plasmon resonance (LSPR) properties. Through FDTD simulations and experimental validation, we demonstrated the superior performance of these flexible plasmonic films in terms of resonance behavior, light-matter interaction, and their ability to resist external environmental influences. The fabricated films exhibited high reflectivity and robust plasmonic resonance modes, indicating their potential for applications in flexible electronics, sensors, and optoelectronic devices. Overall, this work introduces a practical method for designing and fabricating flexible plasmonic films with dynamic tunability, paving the way for the development of advanced plasmonic systems that can be easily integrated into various functional devices for a wide range of applications. Summary

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