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Invited Paper

## Effect of sapphire substrate on the localized surface plasmon resonance of aluminum triangular nanoparticles

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### ABSTRACT

In this paper, we explore the effect of the sapphire substrate on the localized surface plasmon resonance of Al triangular nanoparticles fabricated by nanosphere lithography. We find an obvious shoulder peak which is rarely noticed before as well as a main peak in the the ultraviolet range of the extinction spectrum. Then the electric field distributions surrounding the single Al triangular nanoparticle have been further investigated by numerical simulation using the finite-difference time-domain method. By analyzing the simulation results, we demonstrate that the two peaks in the extinction spectrum are originated from the hybridization of dipolar and quadrupolar modes when the sapphire substrate exists. And this work may provide a better understanding of the effect of sapphire substrate on the localized surface plasmon resonance properties of aluminum triangular nanoparticles.

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### 1. Introduction

Metal nanoparticles can strongly absorb and scatter light due to their ability to support localized surface plasmon resonance (LSPR), which can introduce strong enhancements of the local electromagnetic fields surrounding the nanoparticles as well as distinguished peaks in extinction spectra [1]. These promising properties of LSPR have been applied in a variety of applications, such as optoelectronic devices [2,3], biological and chemical sensing [4,5], Raman signal enhancement [6] and so on. Over the past decades, extensive investigations of LSPR properties and their applications have been focused on noble metal nanostructures, such as Au and Ag, which exhibit LSPR in the visible and near-infrared ranges [7,8]. Nowadays, emerging applications will require the extension of LSPR toward shorter wavelengths. However, in the ultraviolet (UV) range, the LSPR cannot be excited by noble metals for their interband transition [9]. Instead, Al can support LSPR in this range, and it is considered to be the best metal to obtain plasmonic response in the UV range not only for the reason that its bulk plasmon frequency is high and interband transition is negligible in the UV range but also that it is cheap and widely available [10,11]. Although aluminum is easily oxidized, the

transparent oxidation layer that forms on the surface of Al, about 2~3 nm in thickness, can act as a passivation and protection layer to prevent further oxidation. To date, there is an increasing interest in applications using the LSPR of Al, for instance, LSPR-enhanced UV Raman scattering [12], UV light LED devices [13], UV photo-detection [14,15] etc.

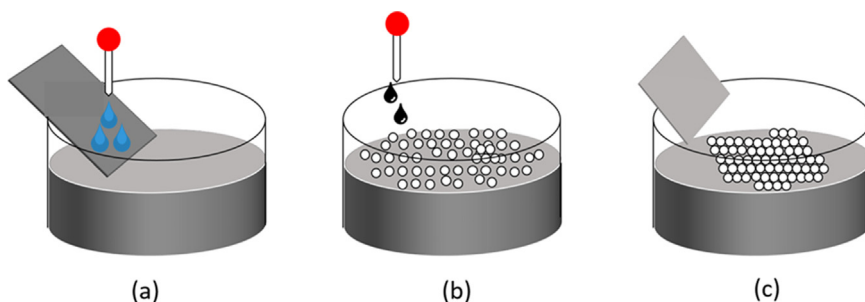
As we know, the LSPR wavelength can be turned over a broad wavelength range by manipulating the size, shape and local dielectric properties of Al nanoparticles [9,16]. And mastering the size of aluminum nanostructures is extremely important in order to tune their LSPR positions in the UV range, requiring proper fabrication technique to prepare such nanoparticles. In addition, as far as we know, there is still a lack of investigations on the effect of substrate on the LSPR of aluminum nanoparticles in the UV range. Therefore it is of great importance to make the effect of substrate clear.

In this paper, we have fabricated Al triangular nanoparticle arrays on sapphire substrate through the nanosphere lithography (NSL) method, which is inexpensive, simple to implement and widely used [17]. And we emphasize on exploring the effect of sapphire substrate on the LSPR properties of as-prepared Al nanoparticles. We find that there is a distinct shoulder peak as well as a main peak in the extinction spectra when the sapphire substrate exists both in the experimental measurement and the numerical simulation. Then we simulate the near-field distributions of the Al nanoparticle with and without the sapphire substrate

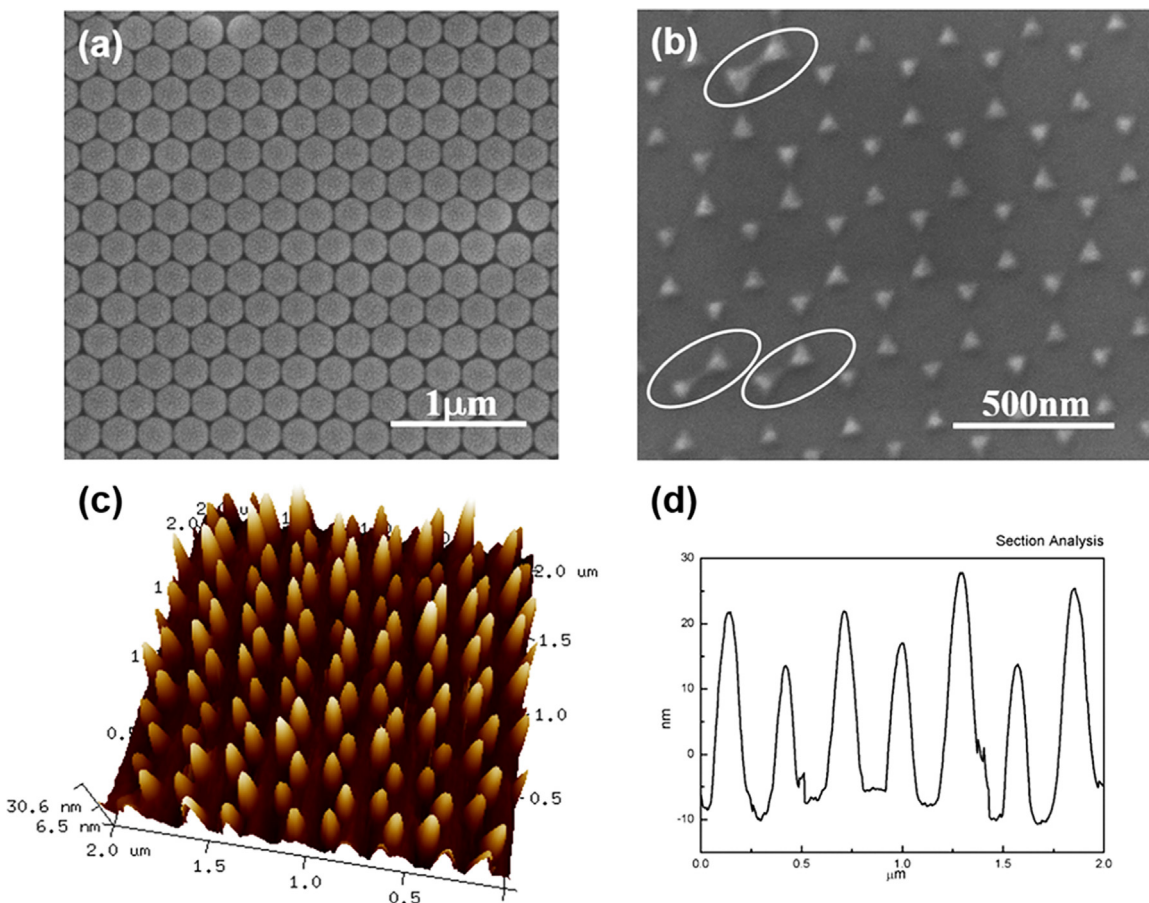
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**Fig. 1.** The fabrication process of PS nanosphere monolayer on the sapphire substrate using the floating- transferring method: (a) dropping prepared PS nanosphere solution on the interface between the glass slides and deionized water; (b) adding sodium dodecyl sulfate solution to consolidate the dispersive nanospheres; (c) transferring the hexagonal close-packed monolayer by the sapphire substrate.



**Fig. 2.** SEM images of (a) as-prepared PS nanosphere monolayer and (b) the fabricated Al nanoparticle arrays on sapphire substrate, large and anomalous Al nanostructures are pointed in white ellipses. (c) 3D morphology and (d) corresponding cross-sectional profile of the Al nanoparticle arrays on the sapphire substrate obtained by AFM measurement.

respectively so as to explain the origin of the shoulder peak. We conclude that the sapphire substrate not only changes local dielectric properties of the Al nanoparticle but also acts as a medium to support the interaction between the different plasmon modes in the Al nanoparticle. We think this work may provide a further understanding of the effect of substrate on the LSPR properties of aluminum nanoparticles.

## 2. Preparation of the Al triangular nanoparticle arrays

We choose sapphire substrate in our experiment because it is transparent in the UV range. Experiments were performed as follows. Firstly, standard cleaning procedures were used to remove

the surface contaminants. And then surface activation employing oxygen plasma was conducted to make the sapphire substrates more hydrophilic. Secondly, polystyrene (PS) nanospheres with diameters of  $260 \pm 8$  nm were coated onto the hydrophilic sapphire substrates by floating-transferring method (illustrated in Fig. 1), yielding a hexagonal close-packed monolayer of PS nanospheres over a large area. Our floating- transferring method is similar to the self-assemble technique in Ref [18]. After drying, the samples were then soaked in heating ethanol at  $70^\circ\text{C}$  for 25 s to decrease the size of the gaps between PS nanospheres, which would act as a mask in the next step. Thirdly, a 50-nm-thick Al (99.99% purity) layer was deposited by e-beam evaporation. After the deposition, the PS templates were removed by toluene. In this way, the Al nanoparticle arrays on sapphire were finally prepared.

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