Applied Surface Science 454 (2018) 270–276

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Quadrupolar plasmon resonance in arrays composed of small-sized Ag nanoparticles prepared by a dewetting method

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ARTICLE INFO

Article history:
Received 16 January 2018
Revised 2 April 2018
Accepted 29 April 2018
Available online 22 May 2018

Keywords:
Quadrupolar resonance
Coupling interaction
Ag nanoparticle
Dewetting
Surface-enhanced Raman scattering (SERS)

ABSTRACT

Quadrupolar plasmon resonances that originate from interparticle near-field coupling interaction were observed in arrays composed of small-sized Ag nanoparticles (∼30 nm). The arrays were prepared by a dewetting process, during which hexagonally arranged aluminum pits were used to induce and confine the nucleation and growth of Ag nanoparticles. With the increase in the thickness of the initial Ag film, the particle size increases, and the interparticle spacing decreases to sub-10 nm scale, making adjacent particles strongly coupled. As a result, the quadrupolar resonance mode occurs, and its wavelength remains practically unchanged, while the dipolar mode shifts toward to a longer wavelength by about 80 nm. In comparison, only a dipolar resonance mode was observed in the non-coupled array that has a large interparticle spacing. The coupled array was demonstrated to exhibit much stronger surface enhanced Raman scattering (SERS) activity than that of the non-coupled array, suggesting that the quadrupolar mode can also be viewed as an indication of strong SERS enhancement in arrays composed of small-sized metal nanoparticles.

1. Introduction

Metal nanoparticles (MNPs) have become the subject of intense research because of their unique optical properties that can concentrate optical fields into subwavelength scale and cause intense light extinction in far-field [1–4]. These fascinating optical properties are originated from the collective electrons oscillation at MNPs surface, known as surface plasmon resonance (SPR), in response to the electrical field of incident light [5]. The plasmonic response of the MNPs can be regulated across a broad spectral range by controlling their composition, shape, size, and dielectric environment, enabling us to tailor the SPR properties for diverse applications [5–8]. Recently, much attention has been devoted to multipolar plasmon resonances due to their distinct plasmonic properties compared to the dipolar ones [9–11]. Theoretical and experimental studies have revealed that the multipolar plasmon modes exhibit narrow line width and large field enhancement [3,9,12,13], which are vital characteristics for the application of MNPs in ultrasensitive biochemical sensing based on localized surface plasmon resonance (LSPR) [3,14] and surface enhanced Raman scattering (SERS) [15–18], as well as in fluorescence [19], nanolasers [20], and others [21,22].

Multipolar plasmon resonances are caused by phase retardation of the electromagnetic field inside the plasmonic nanoparticles [23,24]. The excitation probability of the multipolar plasmons increases with the particle size [25], therefore, they are generally supported by large-sized MNPs. Experimentally, quadrupolar resonances have been observed in spherical nanoparticles with the size larger than 50 nm [19,23,26]. As the particle size increases, the modes shift toward longer wavelength [26,27], and higher order resonance modes, even hexadecapolar resonance, can be excited [27]. Conversely, only a dipolar resonance mode is excited in spherical MNP with the size much smaller than the wavelength of the incident light, in which all electrons in the particle experience roughly the same phase of the incident electromagnetic field [27]. Moreover, elongated metal nanostructures (typically, nanorods) can also support multipolar plasmon resonances [1,9], where the wavelengths of the multipolar resonance modes are dependent on the dimensions of the nanostructures [1,12].

Multipolar plasmon resonances can also be excited through near-field coupling interaction between MNPs in arrays or aggregates [25,28]. When the particles are in close proximity, their local electromagnetic fields associated with the electron oscillations

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https://doi.org/10.1016/j.apsusc.2018.04.266
0169-4332/

overlap and interact on each other, the system becomes coupled [23]. The inhomogeneous electromagnetic field across the particle induced by the adjacent particles mediates the hybridization of the multipolar plasmon modes, rendering the dark quadrupolar mode visible owing to the mixing of the quadrupolar mode with the bright dipolar mode [29,30]. In the coupled array, besides the mentioned particle shape, size, and environment, the interparticle spacing is also critical to determine the plasmonic properties [23,25,28]. Many experiments studied the interparticle coupling in detail, a shift of the dipolar plasmon resonances was generally observed upon decreasing interparticle spacing [23,25,31,32]. Importantly, as the interparticle spacing was further decreased to a distance below 10 nm, strong coupling leads to the appearance of the quadrupolar resonance mode [25,28].

To study the coupling effect between the MNPs, several strategies have been utilized to fabricate two-dimensional arrays composed of MNPs. Among these methods, lithography is ideal to provide a precise control over the size and spacing of the particles, two-dimensional ordered arrays with tunable plasmonic properties can be readily realized [33]. However, this method is expensive and time-consuming for large-area fabrication, especially, it suffers from a difficulty to reduce the interparticle spacing to sub-10 nm scale due to the resolution limit of this technique [25]. Self-assembly, on the other hand, enables extremely small interparticle spacing in arrays [17,32,34], but the usage of ligands during the synthesis and assembly complicates the spectral response of the arrays because of the extreme sensitivity of the plasmon resonances on the dielectric environment [35,36]. Dewetting, that is, deposition and annealing of a thin metal film on a substrate, is the most simple method for the production of metal nanoparticle arrays [2,37,38]. Moreover, this method can readily realize large-area preparation with low cost, and ordered arrays can also be attainable with the assistance of a proper template [37,38].

In this paper, large-area coupled and non-coupled Ag nanoparticle arrays with very small particle size (~30 nm) were prepared by annealing Ag films on structured Al substrates. The effects of the particle size and interparticle spacing on the optical response were investigated, and the SERS activities of these two types of arrays were compared to reveal the significant role of the coupling effect. The results reported here provide a deeper insight into the plasmon resonances supported by metal nanoparticle arrays, and offer possibilities to tune the spectral response toward specific applications via near-field coupling.

2. Experimental details

Ag nanoparticle arrays were prepared by annealing the Ag films that were deposited on structured aluminum substrates with ordered pit arrays. Fig. 1 schematically illustrates the experimental procedure employed in the preparation. Briefly, anodic aluminum oxide (AAO) templates with different hole diameters were prepared by anodizing of high-purity aluminum substrate (99.99% purity) at different voltages in 0.3 mol/L oxalic acid solution. Then structured aluminum substrates with shallow pit arrays were obtained after removing the porous alumina layer in an etchant mixture of 6 wt% H_3PO_4 and 1.5 wt% H_2CrO_4 at 65 °C for 4 h. Subsequently, a layer of Ag film was deposited onto the Al substrate using an ion-sputter coater. After that, annealing was carried out under vacuum in a tube furnace at 450 °C for 120 min. Ag nanoparticle arrays with different structure were then obtained depending on the thickness of the Ag film and the size of the Al pits.

Surface morphologies of the Ag nanoparticle arrays were characterized using scanning electron microscopy (SEM, Hitachi S-4800). The diameters and the interparticle spacings were extracted from the SEM images using Nano Measurer software, 100 particles and 100 gaps were measured for the statistics. Absorption spectra were measured using a UV–vis spectrometer (Shimadzu UV-3600) equipped with a 60 mm-diameter integrating sphere. During the measurements, the array was put at the entrance of the integrating sphere, and the diffuse reflection light was collected and analyzed.

For surface enhanced Raman scattering test, Rhodamine 6G (R6G) was selected as probe molecules. Ag nanoparticle arrays were immersed in the R6G solutions with different concentrations for 3 h and then rinsed with deionized water to remove physically adsorbed molecules, followed by blow drying with nitrogen. The SERS measurements were performed at room temperature on a Raman system (HORIBA Jobin Yvon, LabRAM HR) using a 514 nm Ar^+ laser line for excitation. Before the Raman measurement, the spectrum was calibrated with crystalline silicon.

3. Results and discussions

After the removal of the porous alumina layer, a structured Al foil with bowl-like pits on the surface was formed, as shown in Fig. 2a. These pits arrange into a hexagonal array, the average diameter is approximately 200 nm. The surfaces of the pits are rough, many nano-sized protrusions can be seen on the sidewall and bottom. After sputtering Ag for 200 s on this structured Al substrate, a continuous Ag film that conformally covers the pits surface was formed (Fig. 2b). The Ag film appears golden in the pit array region after annealing, as indicated by the white circle in the inset in Fig. 2c, implying that a uniform nanostructure array forms which supports plasmon resonance [5]. One can see from the SEM image (Fig. 2c) that high density Ag nanoparticles evenly bestrew on the substrate surface, and no large aggregation is found. The high-resolution image shown in Fig. 2d further reveals that a large number of Ag nanoparticles with small size randomly spread on the pits surface and on the ridges between the pits, resulting to very small interparticle spacings. On the contrary, the Ag film deposited on a polished silicon substrate that subjected to the same annealing shows a randomly distributed Ag nanoparticle array with a broad size distribution and a large average interparticle spacing (inset in Fig. 2d), indicating that the surface topography of the substrate has significant effect on the morphology of the resulted Ag nanoparticle array. We think that the nano-sized protrusions on the pits surface can act as nucleate sites to induce the nucleation of Ag nanoparticles during annealing, while random nucleation occurs on the polished silicon surface, resulting in the structural difference of the arrays on these two substrates. Fig. 2e and f show the statistical results of the particle diameters and the interparticle spacings of the array formed on the structured Al substrate. The average diameter and the interparticle spacing of the Ag particles are 21.7 ± 5.5 nm and 10.3 ± 2.3 nm, respectively. By changing the sputtering durations of Ag, a series Ag nanoparticle arrays, denominated as Type 1 arrays, were prepared. The statistical particle sizes and interparticle spacings are listed in Table 1, from which we can see that the size continuously increases with prolonging Ag sputtering duration (i.e. increasing Ag film thickness), correspondingly, the interparticle spacing decreases, falling into sub-10 nm scale.

On the other hand, when we sputtered a Ag film on a structured Al substrate with a very small average pit diameter of 30 nm, an ordered Ag nanoparticle array was then observed after annealing, as shown in Fig. 3. In this case, only a single particle locates at the bottom of each pits, these particles arrange into an ordered hexagonal array, being consistent with the pit array of the substrate. We suggest that the fine particles within a pit are prone to coalesce into one large particle during annealing due to the very small spacing, meanwhile the ridges around the pits act as an effective barrier to restrict further coalescence of the particles in