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Hot spots engineering in hierarchical silver nanocap array for surface-enhanced Raman scattering

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ABSTRACT

We proposed a rapid, simple and room-temperature method to fabricate hierarchical silver nanocap arrays, in which hot spots could be facilely engineered on three-dimensional curved surface. Both optical property and surface-enhanced Raman scattering (SERS) activity displayed non-monotonic Ag thickness dependence. Furthermore, the simulation results obtained by finite-difference time-domain (FDTD) method reveal that hot spots intensity and density on three-dimensional curved surface significantly vary and strongly depend on deposited Ag thickness. The investigation opens a possibility for facile fabrication of SERS substrate with promising hot spot engineering on three-dimensional surface and extremely high SERS activity.

1. Introduction

Local electromagnetic field enhancement effects within the diverse metal nanostructures have been extensively studied and applied in various fields, such as nano-optical devices [1], chemical and biological sensors [2] and surface-enhanced Raman scattering (SERS) [3–11]. It is well known that strong local electromagnetic field enhancement at particular sites, i.e. the 'hot spot' that is in the interstitial regions or the gaps among closely spaced nanostructures allow extremely sensitive SERS detection, even identification of single molecules under ambient conditions [5,6]. Thus, improving intensity and density of hot spots are of crucial importance for designing and fabricating SERS substrates. Several strategies have been proposed for generating and refining hot spots within diverse metal nanostructures, such as dimer-like nanoparticle aggregation [3–6] and dense metallic nanostructure arrays [7–10]. Although extremely intense hot spots exist within dimer-like nanoparticles aggregation [4–6], the uniformity and reproducibility of hot spots and corresponding SERS enhancement are hardly achieved. In contrast, hot spots' intensity and density within two-dimensional metallic nanoparticle array could be significantly increased by precisely controlling the geometry of array, especially the interparticle distance and the uniform, reproducible and high SERS enhancement could be obtained [7–10]. To further increase hot spots' intensity and density, a few of complex array structures with a large three-dimensional surface area available for the formation of hot spots have been exploited [11,12]. Nevertheless, hot spots engineering on three-dimensional surface remains still a challenge due to the complexity of fabrication procedure and the difficulty of hot spot controlling.

Recently, as a new template for fabricating SERS substrates, porous anodic aluminum oxide (AAO) template prepared by hard anodization (HA) technique has attracted the attention of materials scientists [13,14]. Compared with mild anodization (MA) AAO template used extensively in SERS substrate [7–10], HA AAO template offers several advantages for mass production of SERS substrate, such as very fast fabricating procedure, larger period and facile to form free-standing template [15]. However, to the best of our knowledge, HA-AAO template has rarely been used to fabricate SERS substrates with hot spots engineering on three-dimensional surface.

In this article, we proposed a rapid, simple and room-temperature method to fabricate hierarchical silver nanocap arrays, in which hot spots could be facilely engineered on three-dimensional curved surface. The arrays were obtained by electron beam evaporating Ag onto barrier layer surface of HA-AAO template and consisted of hexagonal ordered submicrosized caps with evenly distributed small nanoscale Ag particle on cap surfaces.

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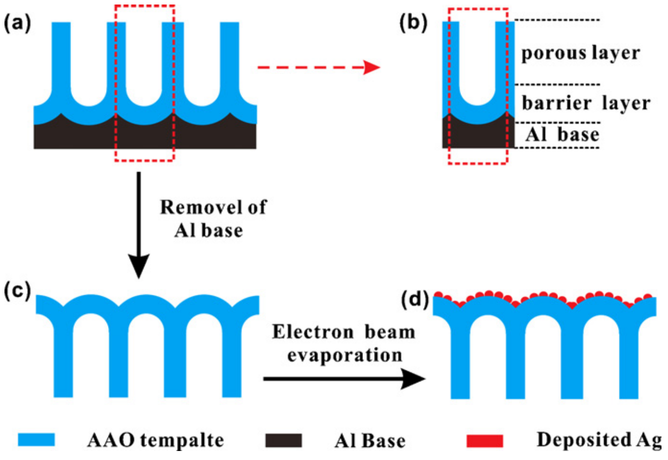

Fig. 1. Schematic flow of fabrication process of hierarchical silver nanocap array (a) HA-AAO with aluminum base; (b) structure diagram of HA-AAO; (c) barrier layer template; (d) hierarchical silver nanocap array.

With the increasing of deposited Ag thickness, the cap surface roughness varied over a wide range and nanoscale gaps gradually became narrower until disappeared. Both optical resonance property and SERS activity displayed non-monotonic Ag thickness dependence. Furthermore, local electric field intensities for hierarchical nanocap arrays have been simulated using the finite-difference time-domain (FDTD) method, which help us to understand hot spot engineering on three-dimensional curved surface.

2. Experiment

2.1. Preparation of hierarchical silver nanocap arrays

Schematic procedure for the fabrication of hierarchical silver nanocap array based on HA AAO template is showed in Fig. 1. The HA AAO template was prepared by two-step HA technique [15] in 0.3 M oxalic acid solutions at 130 V and −1.5 °C for 30 min (Fig. 1(a)). The structure of HA-AAO is schematically shown in Fig. 1(b). Remain aluminum base of HA-AAO templates were then was removed in a saturated $HgCl_2$ solution to obtain barrier layer of HA-AAO substrates (Fig. 1(c)). The barrier layer morphology of as-fabricated HA AAO template measured by atomic fore microscopy (AFM) is showed in Fig. S1 (see Supporting Information). The hierarchical silver nanocap arrays were fabricated by electron beam evaporating various thicknesses Ag from 20 nm to 200 nm onto the barrier layer surface of HA AAO template at the rate 0.2 nm/s in a vacuum of approximately 3×10^{-3} Pa. The temperature of HA-AAO template during evaporating was kept at room temperature (300 K). The schematic cross-section of hierarchical silver nanocap array is showed in Fig. 1(d).

2.2. Characterization of silver nanocap arrays

Field-emission scanning electron microscope (JOEL JSM-6700F) was employed to characterize the surface morphology of hierarchical silver nanocap arrays. Optical absorption spectra were measured in the visible region using UV Spectrophotometer (PE Lambda 750). Raman and SERS spectral measurements were carried out with confocal Raman spectrometer (Horiba Jobin Yvon HR800) with 633 nm excitations. Rhodamine 6G (R6G) was adopted as the analyte for SERS signals measurement. The SERS-active substrate based on hierarchical silver nanocap arrays were immersed in 10^{-5} M/L R6G ethanol solution for 2 h and then thoroughly rinsed with DI water to ensure the same surface coverage for monolayer R6G molecules adsorbed onto different substrates.

3. Result and discussion

3.1. Tunable hierarchical surface roughness by controlling Ag deposition thickness

SEM images of hierarchical silver nanocap arrays are shown in Fig. 2. From the SEM images, the silver hierarchical nanocap array could be described as a submicro-/nanoscale system, namely the submicrosized cap-shaped Ag particles (or building blocks) with nanoscaled surface roughness are in a hexagonal periodic arrangement. The nanoscaled surface roughness of cap-shaped Ag particles was formed by distributing small hemispherical Ag nanoparticles uniformly [16] on the barrier side of AAO template. Furthermore, it is showed that the nanoscale surface roughness of cap-shaped unit strongly depend on the deposited Ag thickness. At the initial stage of silver deposition, only very small Ag nanoparticles were approximately well distributed over the barrier side of AAO template with large interparticle separation (Fig. 2(a)). Then, with the increasing of deposited Ag thickness, these small Ag nanoparticles grew up in size and aggregated gradually along with the decrease in size of gap and increase in surface roughness, which are showed in Fig. 2(b). As the deposited Ag thickness reached a specific value (80 nm in our experiments), the highest surface roughness with the narrowest gap were obtained (Fig. 2(b)). It will be demonstrated in later section that the hierarchical Ag nanocap array with the roughest topography is of the highest SERS activity. However, as deposited Ag thickness reached 120 nm, Ag nanoparticles began to coalesce and the surface roughness apparently decreased, as shown in Fig. 2(c). When deposited Ag thickness was larger than 120 nm, the surface roughness further decreased and gap even disappeared with the increase in deposited Ag thickness. Eventually the smooth nanocap array was formed as the Ag thickness reached several hundred nanometers, as shown in Fig. 2(d). It should be pointed out that all metallic nanostructure arrays were fabricated at room temperature, which is favorable for mass production of SERS substrates and distinctly different from our previous work [10] for fabrication of complex patterned Ag nanoparticle arrays at 473 K. This difference may be attributed to different surface properties [10,17] between HA AAO and MA AAO template.

To further reveal the geometric structure feature of fabricated hierarchical nanocap arrays, the SEM images have been analyzed through precise edge detection by digital image processing technique and the results are showed in Fig. S2 (see Supporting Information). It showed that with the increase in deposited Ag thickness (40–80 nm), the diameter of hemispherical Ag nanoparticle varies considerably (14–22 nm) while the count is almost invariant.

3.2. Non-monotonic behaviors of optical property and SERS activity

The optical properties and SERS activity were investigated by measuring the absorption spectra and SERS spectra and the results are shown in Fig. 3. Fig. 3(a) shows a non-monotonic shift of absorption peak in the visible region with the increase in the deposited Ag thickness. For the deposited Ag thickness smaller than 120 nm, the absorption peak is red-shifted significantly with the increase in deposited Ag thickness. Considering variation of nanoscale Ag nanoparticle diameter and interparticle gap during Ag depositions (Fig. 2(a) and (b)), this red shift could be attributed to increase of hemispherical Ag nanoparticles diameter [16] and the reduction of interparticle gap, which strengthens the coupling between