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Highly ordered Au-Ag alloy arrays with tunable morphologies for surface enhanced Raman spectroscopy

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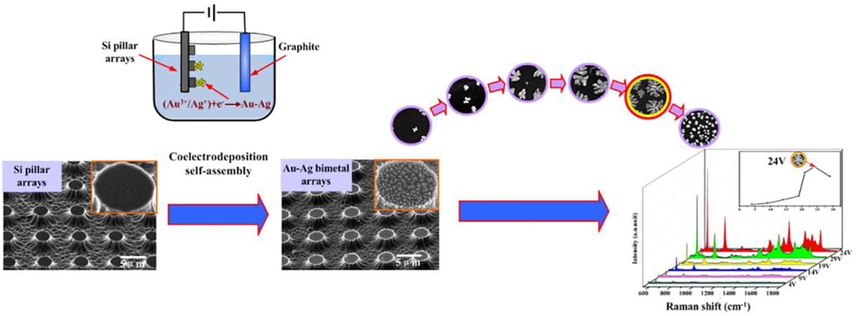
HIGHLIGHTS

- A flexible approach for fabricating the highly ordered Au-Ag alloy arrays for SERS is proposed.
- The morphologies of the Au-Ag alloy are regulated via adjusting the nucleation and growth processes.
- The maximum SERS is observed for the flower-like Au-Ag alloy with a small amount of Au (12%).

GRAPHICAL ABSTRACT

Highly ordered Au-Ag alloy arrays with tunable morphologies for SERS substrates are fabricated by a controllable and reproducible approach combining electrochemical reaction self-assembly and photolithography.



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ABSTRACT

A simple approach combining electrochemical reaction self-assembly and photolithography has been proposed for the controlled and reproducible fabricating the highly ordered Au-Ag alloy arrays for SERS. The nucleation and growth processes of the Au-Ag alloy are adjusted easily via changing the applied voltage and reaction time to obtain the flower-like hierarchy nanostructure, which show the strongest SERS properties due to the wealthy Raman "hot spots" provided by the corners and edges in much-branched flower structure. Moreover, the maximum SERS is observed for the Au-Ag alloy with a small amount of Au (12%), which can lead to a charge separation and favor the probe molecules adsorption to the silver domains. By using these flower-like Au-Ag alloy arrays, the Rhodamine 6G (R6G) with the concentration of as low as 10^{-12}M can be detected easily in this study, which would be very promising for the applications in biosensors and nanodevices with molecule-level detection.

1. Introduction

Since Surface-Enhanced Raman scattering (SERS), where a Raman signal is strongly enhanced when molecules are attached to the rough surface of some noble metal nanostructures, was observed in 1970s [1], there has been a tremendous amount of researches focused on SERS due

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to its single-molecule sensitivity and excellent fingerprint effect for practical applications in detection and recognition technology [2–4]. Generally, SERS-active substrates have been restricted to some noble metals materials, especially the Silver (Ag) and Gold (Au), which have been widely used in SERS studies due to the higher plasmonic enhancement and better biocompatibility [5–9]. Compared with the single metallic Ag substrate with weak stability against oxidation, and Au with the relatively weak SERS activity, Au/Ag alloy materials system is a preferable choice and very promising for the enhancement of SERS signal and application in analytical technique, because it exhibits both the dramatic Raman enhancement and good compatibility [10].

In addition to further optimize SERS effect, recently, benefiting from the advance in micro/nano - fabrication techniques, patterned noble metal arrays substrates applied for SERS have attracted much more attention [11–12]. Compared with the flat noble metal, the metallic arrays can provide broadband, wide-angle and large electromagnetic (EM) fields excitation and surface plasmon resonances (SPRs), and hence to process much more Raman “hot spots”, which can significantly amplify Raman scattering intensity of the attached molecules [13–16]. At present, a variety of SERS arrays substrates have been fabricated by different approaches including nanosphere lithography (NSL), electron lithography technique and anodic aluminum oxide (AAO) template method [17–18]. In comparison, photo-lithography is a simple, low-cost and easy available route for fabricating a uniformly high-ordered and large scale microstructure arrays [19], by which the periods and morphologies of noble metal arrays can be tuned flexibly combining the electrodeposition self-assembly [20–21].

In this paper, we present a simple approach for fabricating the highly ordered Au-Ag alloy arrays in silicon pillar substrates by photolithography and coelectrodeposition self-assembly, and subsequently demonstrate the good control in the morphologies of the Au-Ag alloy structure by means of adjusting the nucleation and growth processes via changing the applied voltage and reaction time. In particular, the Au-Ag alloy prepared can grow tightly on the silicon pillar substrate, which can be recycled after being cleaned in the organic solvent. Moreover, large scale silicon pillar substrates can be obtained very quickly by photolithography and XeF_2 dry etching, where the highly selective isotropic Silicon etch rates are 1–2 μm per minute. Therefore, we think that our result provides a new approach towards ordered arrays of alloy plasmonic structures and makes a demonstration of the emergent application of photolithography and coelectrodeposition self-assembly in SERS substrates for single-molecule detection.

2. Experimental

The fabrication procedure for the Au-Ag alloy arrays can be seen in Fig. 1 (a) and the detail process is as follows: Firstly, a layer of photoresist (AZ MiR (TM) 701 Photoresist) is coated on silicon wafers by spin coating, and then baked at 90 °C for 15 min. After being exposed in a mask aligner (MJB 3, SUSS MicroTec), the silicon wafer coated by photoresist is immersed in developing solution (AZ 300 MIF developer, Made in South Korea) and rinsed by deionized water. Subsequently, a XeF_2 dry etcher systems is adopt to isotropically etch the silicon for less than one minute, and then the high ordered silicon pillar arrays are obtained after cleaning up the residual of photoresist by acetone. Finally, the Au-Ag alloy grows on these silicon arrays by coelectrodeposition and self-assembly with the $HAuCl_4$ and $AgNO_3$ mixed aqueous solution as electrolyte. The morphologies of Au-Ag alloy have been tailored by controlling the nucleation and growth processes through careful regulation of reaction rate via changing the applied voltage and reaction time.

The morphology of the Au-Ag alloy arrays are characterized by a scanning electron microscope (SEM: SU8010, Hitachi), and the effect of morphology on the SERS properties are demonstrated by measuring the Raman spectra of alloy arrays with different morphologies using a HORIBA Jobin Yvon LabRAM HR Evolution cofocal microprobe Raman spectrometer with the 532 nm He-Ne Laser line at room temperature and the diameter of the focused laser spot is about 2 μm. Samples for SERS are dipped into the Rhodamine 6G (R6G) aqueous solution with concentrations of 10^{-5} M for 10 h, followed by thorough rinsing in deionized water to remove the unbound R6G molecules and dry before SERS measurement.

3. Results and discussion

Fig. 1(b) shows the highly ordered silicon pillar arrays fabricated by photolithography and dry etching, with the smooth surface and extremely rough groove bottom. Owing to the superhydrophobic properties of the silicon pillar as the coelectrodeposition electrode (the contact angle (CA) is about 109.3°, as shown in the S1), air pockets are trapped inside structural gaps [22], which cause the restrictive contact between electrolyte and pillar tops. Thus the dendritic Au-Ag alloy can be reduced and assembled mostly upon the pillar top surfaces, while few fragmentary alloy nano dots can be obtained on the bottom of the arrays. The measured EDS mapping indicates that the distribution of the Ag and Au element is uniform as shown in the S2 in the Supplementary Material.

In this process, preferential growth of Au - Ag alloy arrays on silicon pillar structure has been investigated by changing the applied voltages, as shown in Fig. 2.The voltage of Fig. 2(a), (b), (c), (d), (e) and (f) is 4 V, 9 V, 14 V, 19 V, 24 V and 29 V, respectively. It is obvious that the applied voltage plays a powerful role in the growing process of Au-Ag alloy. According to the diffusion limited aggregation (DLA) model, during the reduction and growth process, aggregation number and size can determine anisotropic morphology of Au-Ag alloy [23–24]. As seen from the Fig. 2, when the voltage is low such as less than 4 V (Fig. 2(a)), due to the insufficient electrons provided and low nucleation speed, few Au-Ag alloy can be deposited on the silicon substrate. With the increasing of applied voltage, more and more electronics obtained obviously facilitates the nucleation and isotropic growth of the Au-Ag metal and uniform alloy arrays with flower-like hierarchy nanostructures form (as seen in Fig. 2(e)). However if the voltage is as high as 29 V, the nucleation is instantaneous, and massive metal ions are reduced to atoms, which can accelerate the isotropic growth steps, thereby isolated island Au-Ag alloy grain is formed as shown in Fig. 2(f).

The morphology evolution of Au-Ag alloy is a time-dependent process, as shown in the Fig. 3(a)-(d), the respective coelectrodeposition time is 5, 15, 25 and 30 min with the concentration of $HAuCl_4$ and $AgNO_3$ solution are 0.001 mM and the applied voltage is 24 V. Driven by the high enough voltage, The alloy ions near the cathode obtain the electrons and then to be reduced in the lowest energy part of the Si surface. With the increasing of the reaction time, these reduced alloy particles will grow and ripen, and the difference of alloy atoms on different crystal surfaces results in the increasingly visible anisotropic growth. Thereby flower-like alloy become bigger and denser (as shown in the Fig. 3(a)-(c)). At last, when the time is long enough (over 30 min), there are a few ripened tremendous dendrite, there is probably abnormal grain growth phenomenon of Au-Ag alloy and this tends to form a few ripened tremendous dendritic structures, which will restricts the growth of the surrounding Au-Ag alloy particles as seen in the Fig. 3(d). These extremely large dendritic structures cannot stick to the silicon substrate firmly. Therefore, in our experiment, the deposition time is controlled less than 30 min.

As SERS substrates, the flower-like Au-Ag alloy arrays prepared exhibit strong SERS effect by using 10^{-5}M R6G as probe molecules which can be observed from Fig. 4(a) and (b) corresponding to different applied voltages from 4v to 29 V. Firstly, the contrast curve of the alloy arrays prepared on the Si pillar substrates and the flat Si wafer in Fig. 4(a) shows that the arrays present much stronger Raman signal, which is because that the extremely rough surface of alloy arrays can