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Nanocap array of Au:Ag composite for surface-enhanced Raman scattering

Yongjun Zhang [a,*], Cong Wang [a], Jinpeng Wang [b], Lei Chen [a], Jia Li [a], Yang Liu [a], Xiaoyu Zhao [a], Yaxin Wang [a], Jinghai Yang [a,c]

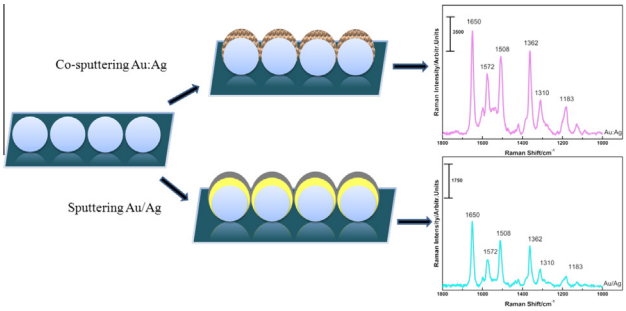
[a] Key Laboratory of Functional Materials Physics and Chemistry, Jilin Normal University, Ministry of Education, Siping 136000, PR China
[b] Northeast Forestry University, Material Science and Engineering Institute, Harbin 150040, Heilongjiang, PR China
[c] Key Laboratory of Excited State Physics, Changchun Institute of Optics Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, PR China

HIGHLIGHTS

- The co-sputtering Au:Ag bimetal array formed the protrusion network of Ag and Au nanoparticles.
- The metal protrusions in the waxberry-like shell contribute to the Raman enhancement.
- The SERS enhancements show the strong gap size-dependent behaviors.

GRAPHICAL ABSTRACT

In comparison to the curved Au/Ag bilayer, the Au:Ag bimetal arrays exhibit 4-fold more enhancement when Rhodamine 6G is chosen as the probing molecule.



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ABSTRACT

We fabricated Au:Ag nanocap arrays by co-sputtering Au and Ag onto two-dimensional polystyrene (PS) colloidal sphere templates in a magnetron sputtering system for the surface-enhanced Raman scattering (SERS) substrate. In contrast to the bilayer Au/Ag, the co-sputtering Au:Ag bimetal array formed the protrusion network of Ag and Au nanoparticles, which contributed to Raman enhancement in the waxberry-like structure. The metal protrusions formed waxberry-like shell in which the PS beads were encapsulated. At the same time, the Au:Ag bimetal arrays exhibit 4-fold more enhancement in the SERS signal intensity of Rhodamine 6G at the 1649 cm^{-1} than Au/Ag bilayer array, which is ascribed to the plasmon coupling between the nanoparticles of Au and Ag on the sample. When the PS colloidal particle templates were etched by O_2-plasma before sputtering process, the nanogaps affected the surface plasmon resonance (SPR), and the optimal gaps between adjacent Au:Ag nanocaps generated even stronger SERS enhancements. This SERS substrate of Au:Ag showed high sensitivity and reproducibility. The EF of Au:Ag nanocap array substrate onto which Rhodamine 6G (R6G) were adsorbed was evaluated as 6.72×10^{10}.

1. Introduction

Surface-enhanced Raman scattering (SERS) is the one of the most effective detection methods for its high sensitivity, rapid

* Corresponding author.
E-mail address: jhyang1@jlnu.edu.cn (Y. Zhang).

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response, noninvasive analysis, and fingerprint recognition [1–4]. There are two mechanisms to the enhancement of SERS, one is the chemical mechanism (CM) and the other is the electromagnetic mechanism (EM). The EM is considered as the main mechanism as the CM contributes merely 10–10^4 to single molecule enhancement while the EM gives 10^8 enhancement or even more. In the presence of plasmonic surface structures the EM fields can amplify the Raman scattering intensity due to surface plasmon resonance (SPR). SERS processes based on SPR have been widely used for the molecular recognition of chemicals and biomolecules [5]. A lot of articles have focused on optimizing the surface patterns of orderly arrayed metallic nanostructures. SPR can be tuned by adjusting the shape, size, environment, composition, and the nanogap in the metal nanostructure arrays [6–11]. Among these characteristics, the nanogap in the metal nanostructure arrays is one of the most significant factors for SERS responses because the coupling among adjacent metal nanostructures can amplify the local EM field enhancement [12–15]. Theoretical studies have shown that variations in particle–particle spacing affect the strength of these "gap plasmons" between nanoparticles. When the spacing sizes change as small as 1 nm, the SERS signal rise or fall by amounts as large as an order of magnitude [16,17].

However, the nonuniform distribution of "hot spots" and the randomly roughened metal surfaces that result in inhomogeneous distribution of target molecules provide challenges to obtaining SERS performance. Until today, a simple and reproducible method to fabricate metal nanostructures over a large area with high uniformity remains a major issue, and the studies on the reproducibility and uniformity of SERS substrates are concentrated on advanced nanopatterning techniques such as electron-beam lithography [18], electro-chemical metal growth [19], nanoimprint lithography [20], nanosphere lithography (NSL) [21–27], and so on. Compared to other methods, nanosphere lithography (NSL) is an economic, robust route and simple method for the fabrication of uniformly ordered nanostructure array over large area owing to its good wide size ranges, easy availability monodispersity [28–31]. In our previous reports, we fabricate the ordered nanogap arrays over large area by NSL and the approach could be extended to a wide range of coating materials, allowing controlled nanocap thickness and size, the size of the nanogap [32].

Since the discovery of SERS for the EM mechanisms about 30 years ago, the noble metal silver (Ag) and gold (Au) have been the promising materials as SERS-active substrate due to their remarkable surface plasmon characteristics. Ag is known to be the most effective metal for Raman signal enhancement due to its excitation being in the visible part of the electromagnetic spectrum. However, Ag is not regarded as a bio-compatible and stable material due to its strong oxidizing power [33]. In contrast, Au is a typical bio-compatible and chemical performance is stable material, but its SERS signal enhancement is relatively weaker than that of Ag.

In this paper, we fabricate a large-area, highly ordered Au:Ag nanocap array by co-sputtering Au and Ag onto two-dimensional PS colloidal particle templates in a magnetron sputtering system, and the Au:Ag nanocap arrays show good surface uniformity over large areas and size-dependence. When the PS colloidal particle templates are etched by O_2-plasma, the nanogap between nanocaps can be controlled by etching time. The large-area, highly ordered, and stable Au:Ag nanocap arrays lead to a large enhancement of SERS activity.

2. Experiment

2.1. Materials

Rhodamine 6G (R6G 96%) was obtained from Aladdin, 4-aminothiophenol (PATP), Sodium dodecyl sulfate and ethanol were purchased from Sigma–Aldrich Co., Ltd. at highest purity available and used as received without further purification. Au and Ag targets were purchased from Beijing TIANQI Advanced Materials Co., Ltd. (HZTQ). Silicon (Si) wafer and ultrapure water (18.0 Ω cm^{-1}) was used throughout the present study. The monodisperse polystyrene colloid particles were purchased from Duke (10 wt% aqueous solution).

2.2. Assemble of PS arrays

The two-dimensional (2D) ordered array of polystyrene colloids microsphere by self-assemble technique were fabricated on Si wafer. First, keep the thorough washed silicon substrates in 10%

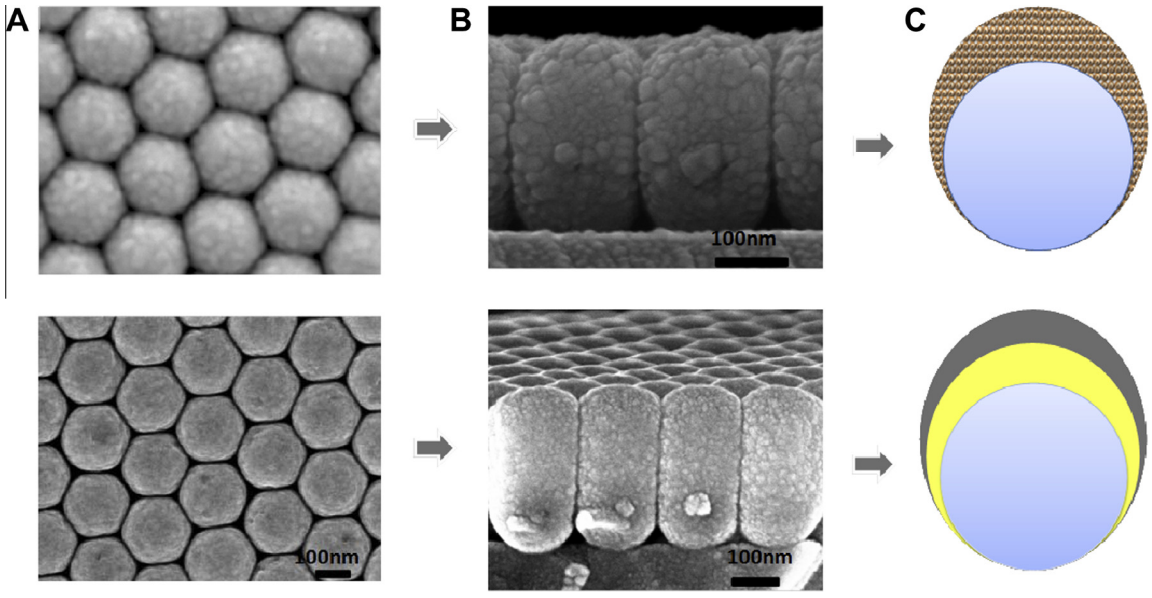

Fig. 1. The schematic diagram and SEM images. (A) The SEM images of Au:Ag nanocap array and Au/Ag bilayer on PS template. (B) The high enlarge SEM image of Au:Ag nanocap array and Au/Ag bilayer on PS template. (C) The schematic diagram of two structures.