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Full Length Article

# High density Ag nanobranches decorated with sputtered Au nanoparticles for surface-enhanced Raman spectroscopy

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ABSTRACT

High density Ag nanobranches (NBs) decorated with Au nanoparticles (NPs) have been fabricated through pulsed electrodeposition using porous anodic aluminum oxide (AAO) as a template, followed by a metal sputtering process. Au NP-decorated Ag NBs show higher surface-enhanced Raman scattering (SERS) intensity than pure Ag NBs due to tiny Au NPs creating additional hot spots which contribute to the increased Raman enhancement. High density Ag NBs protruding from planar AAO templates function not only as an effective plasmonic material but also as an indispensable platform for loading a large amount of Au NPs with a narrow size distribution. Moreover, the long term stability of the SERS substrates significantly improved by decorating Ag NBs with Au NPs resulting in high SERS intensity even after several months of storage in air.



## 1. Introduction

Since its discovery in the 1970s surface-enhanced Raman spectroscopy (SERS) has attracted much attention as a powerful analytical tool for detecting analytes down to the single molecule limit [1,2]. Attaching the analyte molecules to noble metal substrates their Raman signal can increase by several orders of magnitude resulting in a distinct fingerprint characterization of the analyte [3–5]. Although the detailed mechanism of SERS is not fully understood yet, it is widely accepted that the enhancement of Raman signals is attributed to the strong electromagnetic fields induced by localized surface plasmon resonances (LSPR) on the surface of noble metals [6–8]. The electromagnetic fields are largely enhanced at the gaps between the noble metal nanostructures, which are called hot spots [9,10]. For practical applications, plasmonic hot spots with small sizes, high density, and homogeneity in distribution over the whole probe area are important for SERS-substrates. Various approaches have been investigated to fabricate diverse metallic nanostructures as SERS-substrates for stable and reproducible Raman signals using electron beam lithography (EBL) [11–13], focused ion beam milling (FIB) [14–16], and nanosphere lithography [17,18]. However, lithographic processes are commonly complex and expensive, require high accuracy and are time consuming. Template techniques on the other hand are regarded as unique fabrication approaches yielding highly ordered periodic nanostructures on large areas. Several reports of SERS substrates consisting of nanostructures created by anodic aluminum oxide (AAO) templates already exist. Zhulin Huang et al. have fabricated Ag nanoparticle decorated Ge nanocap arrays by ion sputtering on the CVD-grown Ge nanocaps protruding from the planar surface of an AAO template [19]. Bensong Chen et al. have presented a simple and effective synthetic approach for large-area Ag-NP@NiO-NFs@Ni-NR arrays based on the AAO template method. The large quantities of homogeneously distributed Ag nanoparticles a provide high SERS activity mainly arising from the electromagnetic coupling between the neighboring Ag nanoparticles [20]. Yong Lei et al. have demonstrated the preparation of highly enhanced and reproducible SERS substrates of Ag nanoparticle arrays with very small gaps on the basis of the ultra-thin alumina mask technique [21].

One of the important properties investigated for optimized SERS substrates is the composition of the nanomaterials. For example, Ag and Au can be combined as the highly active SERS substrates with novel optical properties [22] because Ag is a more effective plasmonic material than Au, while Au shows clear advantages in terms of chemical stability [23]. Recently, several studies report that Ag-Au bimetallic nanoparticles show higher SERS intensity than the pure Ag or Au nanoparticles, which can be explained by pin-hole theory [24] and the effect of adsorbate-induced aggregation favored at certain Ag-Au ratios [25]. In this work, we report a simple approach to fabricate Au nanoparticle (NP)-decorated Ag

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