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Green synthesis of multi-dimensional plasmonic coupling structures: Graphene oxide gapped gold nanostars for highly intensified surface enhanced Raman scattering

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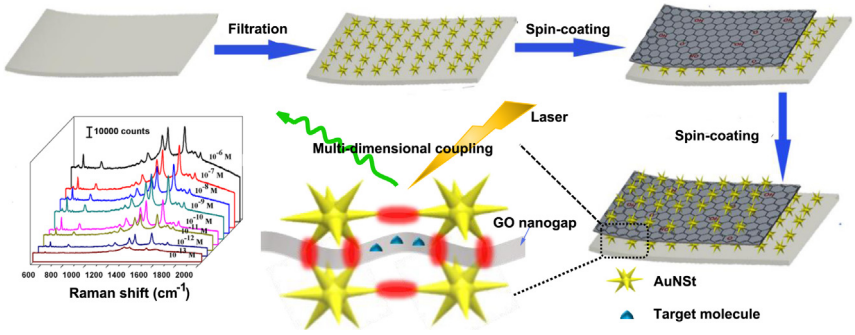
HIGHLIGHTS

- The AuNSt-GO-AuNSt hybrid was fabricated using an environmentally benign approach.
- The hybrid substrates manifest ultra-high sensitivity and excellent re-producibility.
- The substrate was explored for distinguishing detection of food additives.

GRAPHICAL ABSTRACT



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ABSTRACT

Graphene-mediated surface-enhanced Raman scattering (SERS) substrates are currently explored for ultra-sensitive detection and expected to provide uniform SERS response by the virtue of graphene and plasmonic metal nanostructures. Here, we integrated graphene oxide (GO) and anisotropic metal nanostructures to create a novel multiple coupling system, in which ultrathin GO as nanospacer was sandwiched between two layers of closely packed gold nanostars (AuNSts). The sandwiched hybrid was prepared through alternative loading of AuNSts and graphene oxide (GO) film via filtration and spin-coating methods in the absence of any polymer stabilizer or organic linkage agent. The morphologies and plasmon resonance of AuNSts could be tuned by simply adjusting the synthesis parameters. Due to the multi-dimensional plasmonic coupling in horizontally and vertically patterned AuNSts, extra chemical enhancement and outstanding molecule harvesting capability from GO interlayer, the as-prepared AuNSt-GO-AuNSt sandwich structures manifested ultrahigh sensitivity and excellent reproducibility (the signal variations < 6%). A detection limit of rhodamine-6G (R6G) as low as 10^{-13} M and a high enhancement factor of 6.64×10^7 were achieved. Particularly, the AuNSt-GO-AuNSt system was applied to detect erythrosine B and chrysoidin down to 10^{-9} M as well as offer spectroscopic identification in complicated solutions, indicating great potential practical applications for the rapid and sensitive on-site monitoring, especially for food and environmental safety.

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1. Introduction

Surface enhanced Raman scattering (SERS), as a powerful and nondestructive technique in chemical and biologic sensoring applications, has procured utmost attention due to its ultrasensitivity, unique spectroscopic fingerprint and rapid pretreatment [1–4]. It is generally recognized that pronounced SERS signal improvements originate from huge localized electromagnetic field (EM) enhancement at hot spots, which always occur near sharp asperities and nanoscale gaps of plasmonic metal nanostructures [5,6]. Up to now, a great deal of efforts have been devoted to fabricate anisotropic noble metal nanostructures (gold, silver) with high surface roughness, plethora of corners, sharp tips and interparticle gaps to take advantage of their shape and size-dependent plasmonic properties, such as rod-like, polyhedral, dendritic, flower-like, and echinus-like nanostructures [7–12]. Among the numerous noble metal nanostructures, the star-shaped gold nanostructure composing of a central core and multiple protrusions with sharp tips is one kind of attractive SERS platform because of their good biocompatibility, stability and remarkable electromagnetic enhancement from multiple localized surface plasmon resonances (LSPRs) among the tips and core-tips interaction [13]. Moreover, the plasmon resonances of gold nanostars (AuNSts) can be tuned from visible into the near-infrared region by regulating protrusion length, density and tip sharpness, which are beneficial for biological application [14–18]. However, gold-based SERS substrates remain challenging to meet the requirement of practical application, since conventional noble metal substrates including AuNSts still suffer from poor affinity towards organic molecules particularly aromatic pollutants. In this context, hybridization of plasmonic metal nanostructures with graphene or its derivatives (graphene oxide-GO and reduced graphene oxide-rGO), perfect two-dimensional (2D) materials with a monolayer of sp^2 hybridized carbon atoms, is an ideal strategy to significantly improve the SERS performance for aromatic compounds and pesticides monitoring [19–22]. The graphene encapsulated metallic nanoparticles (NPs) and NPs residing on the sheet of graphene/GO have been demonstrated to possess improved SERS sensitivity, stability and stronger capability of enrichment for aromatic molecules [23–30].

Recently, more complicated graphene-plasmonic metal hybrid systems have been developed by exploiting their multi-dimensional plasmonic coupling, where graphene served as uniform sub-nanometer gap for accurately engineering vertically distributed hot spots. Some typical studies involved graphene embedded sandwich hybrids, such as Au NP-graphene-Au NP, Au-graphene-Ag, Ag-graphene-Ag hybridized structures. In these graphene-plasmonic metal combination systems, tremendous near-field enhancement in multiple dimensions, high adsorptivity of graphene for aromatic target molecules and additional chemical enhancement collectively lead to extremely high SERS sensitivity [31–33]. Zhao et al. developed a novel SERS substrate with monolayer graphene sandwiched between gold NPs and silver nanohole arrays for ultrasensitive and high reproducible signal readout. The minimum detected concentration of rhodamine-6G (R6G) was as low as 10^{-13} M [34]. Moreover, GO, chemically modified graphene featuring abundant oxygen-containing functional groups on the basal plane or edges, is also commonly explored to create SERS-active nanogaps for enhancing the multiple dimensional couplings [35,36]. Duan designed and fabricated a sandwiched SERS platform with ultrathin thiolated GO nanosheet embedded between two layers of closely distributed Au@Ag NP arrays. This GO sandwiched hybrids allow for precise position of aromatic compounds or biomacromolecules on the nanogap separated by GO monolayer. Moreover, the combination of multi-dimensional plasmonic couplings, additional chemical enhancement with extraordinary enrichment and accurate position for target molecules empowers the GO-sandwiched SERS substrate for ultrasensitive and multiplex detection of DNA sequences [37]. Besides these graphene-NP sandwiched structures, the graphene-NP film gap systems have also been reported due to its tremendous near-field enhancement and outstanding sensing capability [38]. Consequently, multi-dimensional plasmonic coupling structures have become one of hot research topics for the development of SERS platform in widespread real-world application. However, there is a lack of studies on multiple coupling systems of graphene-anisotropic nanostructures with sharp asperities or multiple branches.

In this work, we provide a facile and environmentally benign approach to fabricate a novel sandwiched AuNSt-GO-AuNSt substrate in the absence of any surfactants and organic additives. High yield AuNSts with tunable morphologies and optical properties were obtained by Ag^+ assisted seed mediated growth method as well as uniformly and densely assembled on the filter membrane using filtration method, serving as the bottom layer. Compact attachment of star-shaped nanostructures could generate numerous active hot spot and promote EM coupling and reproducibility. Then, GO and AuNSt aqueous solution were spin-coated successively to form the interlayer and top layer of sandwiched hybrids. In our design, ultrathin GO film served as nanospacer to create SERS-active gaps with large field confinement and enhancement between two layers of closed attached AuNSt arrays. By integrating the advantages of extraordinary plasmonic properties of anisotropic AuNSts, molecule harvesting capability and extra chemical enhancement of GO, this GO gapped architectures exhibit ultrahigh sensitivity with wide linear response range and excellent reproducibility. Furthermore, the AuNSt-GO-AuNSt substrate can be employed in trace detection and spectroscopic identification of colorants in complex samples, indicating practical applications for on-site monitoring of food and environmental safety.

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$, 98%), chloroauric acid ($HAuCl_4{\cdot}4H_2O$, 99.9%) and R6G were purchased from Alfa Aesar. Ascorbic acid (AA, 99.8%), sodium citrate ($Na_3C_6H_5O_7$, 99.8%), sodium borohydride ($NaBH_4$), sodium iodide (NaI), sodium chloride (NaCl), sodium bromide (NaBr) and microfiltration membrane were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of AuNSts

2.2.1. Synthesis of Ag seed

The gold nanostars were synthesized by a silver-assisted seed-mediated growth method. Briefly, 1 mL of 0.05 mol/L $AgNO_3$ and 1 mL of 5% sodium citrate solution were added into 48 mL ultrapure water and mixed thoroughly under stirring for 5 min. Then, 0.05 mL of $NaBH_4$ (1 mg/mL) was added into the above mixture as the solution color simultaneously turned from transparent to black, and immediately afterwards changed to brownish yellow. The obtained Ag seed solution was centrifuged (12,000 rpm for 15 min) and upper solution were collected for subsequent experiments.

2.2.2. Synthesis of AuNSts

In the typical synthesis of AuNSts, 0.01 mL of as-prepared Ag seed solution was added to 0.3 mM $HAuCl_4$ solution (7.5 mL, 8 mL, 8.5 mL) in a 25 mL glass vial under stirring. Afterwards, 0.001 M $AgNO_3$ solution (0.05 mL, 0.10 mL, 0.15 mL) and 0.05 mL of AA (0.1 mol/L) were added simultaneously and continually stirred for 2 min. Finally, the as-prepared AuNSt solution were centrifuged at 4000 rpm for 15 min and re-dispersed in 1 mL ultrapure water for further use. The plasmonic properties were tailored by adding 0.01 mL of different halogen ions (1 mol/L NaCl, NaBr, NaI).

2.3. Synthesis of AuNSt-GO-AuNSt

AuNSt-GO-AuNSt sandwich hybrids were synthesized by spin-