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Three-dimensional gallium nitride nanoflowers supports decorated by gold or silver nanoparticles to fabricate surface-enhanced Raman scattering substrates

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ABSTRACT

Three-dimensional (3D) metal-semiconductor nanostructures as surface-enhanced Raman scattering (SERS) substrates were designed by *in situ* electrodeposition of gold nanoparticles (AuNPs) or *in situ* photodeposition of silver nanoparticles (AgNPs) on gallium nitride (GaN) nanoflowers (NFs) supports fabricated by metal-assisted photochemical etching of single crystalline GaN. 3D AuNPs/GaN NFs and AgNPs/GaN NFs substrates exhibit excellent enhancement effect for Rhodamine 6G (R6G) due to more "hot spots" in the same probing volume compared to 2D GaN based substrates. The enhancement factors of the AuNPs/GaN NFs and AgNPs/GaN NFs substrates are up to 2.1×10^7 and 5.9×10^7, respectively, and the corresponding detection limits of R6G are 10^{-8} and 10^{-10} M, respectively. Moreover, further study reveals both substrates have good reproducibility and long-term stability. The performance of the prepared substrates for biological application was demonstrated by the detection of bovine serum albumin (BSA). A series of characteristic bands of amides suggest BSA can be well adsorbed on the surface of the AuNPs/GaN NFs and AgNPs/GaN NFs substrates, which demonstrates our substrates have good biocompatibility and are promising candidates for SERS biosensors.

1. Introduction

Surface-enhanced Raman scattering (SERS) spectroscopy has demonstrated its power as an ultra-sensitive and non-destructive analytical tool in various fields including electrochemistry, environmental analysis and biomedical science over the past four decades [1]. To date, the major obstacle of SERS towards practical application is its intrinsic lack of generality and reliability, *i.e.*, poor reproducibility of SERS substrates [2]. Although numerous SERS substrates have been developed to improve enhancement factor, achieve quantitative determination, prolong substrate lifetime and permit SERS studies in diverse environments, at present, it is still difficult to obtain a low cost, stable, sensitive and reproducible SERS substrate [3–8]. As is often the case, according to different application domains, specific SERS substrates are designed to satisfy the relevant requirements. In quantitative analysis, the uniform and reproducible SERS substrate is favorable [9–11]; however, in trace detection, the SERS substrate with the largest enhancement is preferred [12–14]. A clean and good biocompatibility SERS substrate is requested for bio-related detection [15–17].

Essentially, SERS is a surface plasmon enhanced Raman effect, hence metallic nanoparticles (NPs) especially gold and silver are among the most studied SERS substrates due to their unique localized surface plasmon resonance (LSPR). However, the application of dispersed or aggregated metallic NPs as SERS substrates in real analytical environments is limited due to their poor reproducibility and potential sampling challenge [18]. The reproducibility problem can be alleviated by immobilizing metallic NPs on solid supports. Compared with the attachment of pre-prepared metallic NPs on supports through chemical bonding or electrostatic self-assembly methods, the *in situ* growth of metallic NPs on supports *via* chemical or electrochemical reduction approaches are more simple and effective [19–23]. *In situ* deposition can efficiently inhibit the coffee-ring effect [24], moreover, surface contaminants such as linkers or surfactants, which can affect the SERS efficacy and generate extra signals except target molecules, are excluded for *in situ* synthesis process.

Compared to two-dimensional (2D) substrates, 3D substrates are more suitable for SERS. Firstly, 3D substrates have more "hot spots" which can generate greater enhancement. Secondly, 3D sub-

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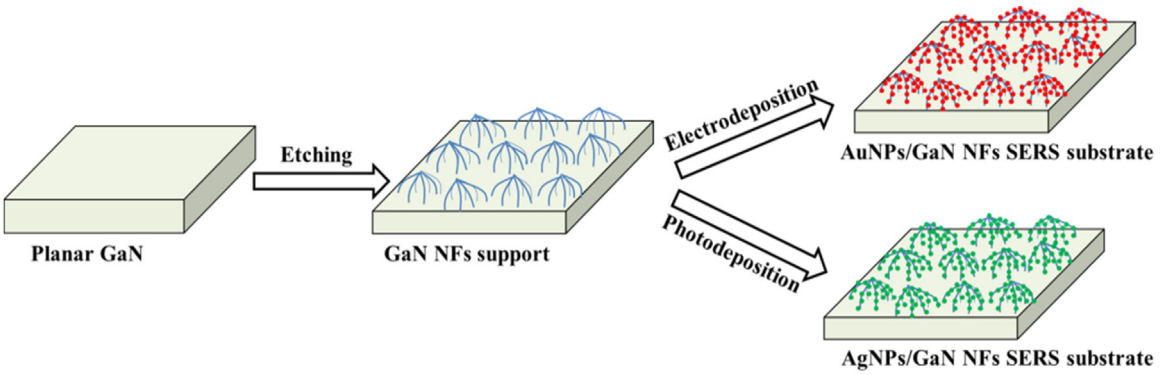

Fig. 1. Schematic route for the fabrication of 3D SERS substrates made of GaN NFs supports decorated with AuNPs or AgNPs.

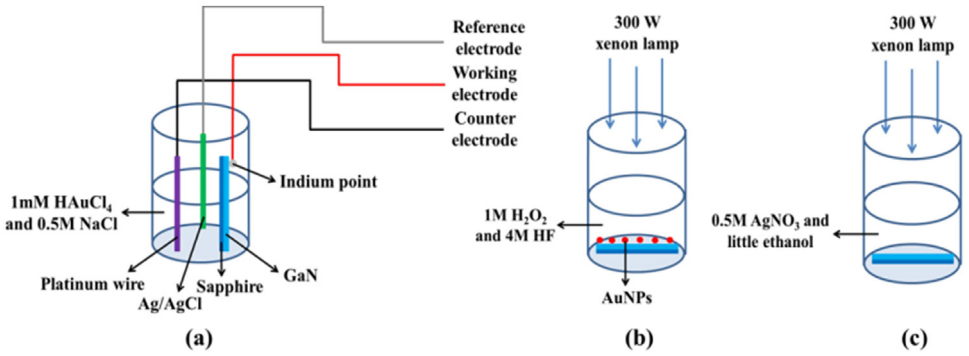

Fig. 2. Schematic diagram of the experimental set ups for the (a) electrodeposition of AuNPs, (b) MaPEtch of GaN and (c) photodeposition of AgNPs.

strates can provide larger surface area, which can interact with more target molecules. Last but not least, the unique geometry morphology under the synergistic effect of metallic NPs and 3D support may supply some extra enhancement [25]. Different types of 3D support materials such as anodic porous alumina [26,27], silicon nanopillars [28] and nanowires array [29], TiO_2 [30] and ZnO [31] nanorods arrays have been reported to fabricate 3D SERS substrates. Such 3D SERS substrates with vertically stacked plasmonic nanostructures can efficiently couple incident photons, which can greatly enhance Raman signals [32].

Metal-semiconductor hybrid systems have been widely explored as SERS substrates to study exciton-plasmon interactions. Gallium nitride (GaN) as a direct wide bandgap semiconductor has been long prized for its optical properties [33]. Recently GaN has garnered increasing attention as significant building blocks for the assembly of sensors owing to its super chemical stability and good biocompatibility [34,35]. Among GaN nanostructures, porous GaN [25,32], GaN nanopillars [36] and nanowall structure [37] have been reported to fabricate SERS substrates. Here, in this work, we describe simple solution approaches to fabricate SERS substrates based on 3D GaN nanoflowers (NFs) supports. The fabrication methods are briefly presented in Fig. 1. First, 3D GaN NFs supports were prepared by metal-assisted photochemical etching (MaPEtch), which has merits of no lattice damage and process simplicity [38]. Then 3D GaN NFs supports were decorated with gold nanoparticles (AuNPs) *via in situ* electrodeposition or silver nanoparticles (AgNPs) *via in situ* photodeposition to fabricate 3D AuNPs/GaN NFs or AgNPs/GaN NFs SERS substrates, respectively. Compared with 2D planar and porous GaN supports, 3D GaN NFs support can contribute to generate stronger Raman signals of Rhodamine 6G (R6G), which reveals the structure-function relationship between substrates and SERS. A series of further study demonstrates 3D AuNPs/GaN NFs and AgNPs/GaN NFs substrates have relatively good reproducibility and long-term stability, which is vital for practical applications. 10^{-6} M bovine serum albumin (BSA) can be detected on both AuNPs/GaN NFs and AgNPs/GaN NFs substrates, which demonstrates our GaN NFs supported substrates can be good substrate candidates for SERS biosensors.

2. Experimental

2.1. Materials

Single crystalline GaN film was grown on *c*-plane sapphire substrate by hydride vapor phase epitaxy. The Si-doped GaN layer was 5 μm thick with a free carrier concentration of 4×10^{18} cm^{-3}. Two-inch GaN wafer was cut into 10 mm × 3 mm samples. The GaN samples were cleaned successively with acetone, ethanol and deionized (DI) water, then dipped in aqua regia for 30 min to remove surface contamination. After that, they were rinsed in DI water and dried with N_2 prior to use. R6G and BSA purchased from Sinopharm Chemical Reagent Co., Ltd were used as the SERS probe molecule and model protein, respectively.

2.2. Fabrication of 3D GaN NFs supports

3D GaN NFs supports were fabricated by MaPEtch technique. AuNPs as metal catalyst were first electrodeposited on the GaN sample by cyclic voltammetry (CV) in a three-electrode cell (Fig. 2a). Indium point was welded on the front side of the GaN sample to form ohmic contact, which was used as the working electrode. Platinum wire and Ag/AgCl were used as the counter and reference electrodes, respectively. Two cycles of CV were carried out from 0.5 to −1.5 V with the scan rate of 50 mV/s. The electrolyte consisted of 1 mM $HAuCl_4$ and 0.5 M NaCl. After the electrodeposition of AuNPs, the MaPEtch process was implemented by immersing the