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Experimental and theoretical investigation for a hierarchical SERS activated platform with 3D dense hot spots

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ABSTRACT

Hot spots generated from the ultra-small nanogaps will tremendously contribute to the strong electromagnetic field. Therefore, the establishment and design of nanogaps are extremely significant. Here, a hierarchical structure, AgNPs/bilayer graphene/Au nanonet, was proposed to form the dense three-dimensional (3D) hot spots and demonstrated in experiment and theory. Numerous nanometer gaps in the complex Au nanonet structure (~8.67 nm) and in AgNPs/Au nanonet isolated by bilayer graphene (0.64 nm) were achieved, which is much beneficial for the obtainment of the hot spots. Based on this surface enhanced Raman scattering (SERS) substrate, an excellent SERS activity (EF ~ 9.1×10^9), high sensitivity (10^{-13} and 10^{-12} M respective for Rhodamine 6G (R6G) and crystal violet (CV)), and SERS signals homogeneity, outstanding reproducibility (maximum intensity deviation from substrate to substrate ~10.43%) were obtained, which can be attributed to the abundant lateral and vertical hot spots introduced by the hierarchical structure. Moreover, the proposed SERS substrate was used to sensitively detect the harmful malachite green (MG), which exhibits a great prospect as a potential SERS sensor in food safety field and biochemical molecules.

1. Introduction

Under the laser irradiation, the light-matter interaction between incident light and mintage metallic surface will motivate surface plasmons that include localized surface plasmons (LSPs) and surface plasmon polaritons (SPPs) [1]. In the former, the coherent oscillation of free electrons existing in nanogaps between metal nanoparticles (NPs) and NPs or thin film can couple with the incident photon and produce the LSPs resonance (LSPR). As we all know, the LSPR effect will result in the tremendous local field enhancement (hot spot) defined as electromagnetic mechanism (EM). Just then, the LSPR contributes to the excitation of SPPs that travel in waves in prolonged metal film interface and makes the localized and extremely spatially structured fields enhancement possible [1–4]. Surface enhancement Raman scattering (SERS), as an extremely powerful spectral tool with such plasmonic effects, was widely investigated [5]. To obtain expected SERS substrates with assist of LSPR and SPPs, the variants of SERS such as the tip-enhanced Raman spectroscopy (TERS) and shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) had been broadly researched, which can greatly improve the SERS enhancement factor (EF) [6,7]. But in these technologies, the materials and thickness of coating shell, as the main roles, are challenging to be formed around the mintage metal (Ag, Au and Cu) core. In addition, some expensive precision instruments are required in the processes above. Therefore, it is greatly vital to find a nanomaterial as sub-nanospacer that can be easily integrated to SERS substrate.

Graphene, a 2-dimension (2D) material closely packed by sp^2 hybridized carbon atoms into honeycomb structure, has drawn extensive attentions due to the unique properties and has been applied in various aspects including SERS [8]. Graphene can be fabricated by chemical vapor deposition (CVD) on the centimeter large of Cu foil [9]. Monolayer (0.34 nm) graphene can be transferred to arbitrary target substrate by the wet-etching method, which is a simple and easy solution [10–12]. What's more, it has been demonstrated that graphene can be used in SERS, which can act as chemical mechanism (CM) enhancer, absorbent toward target molecules and protective layer by virtue of chemical inertness [13].

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Recently, some structures introduced nanogap by graphene, which can skillfully be assembled into nanoparticles (NPs)/graphene gap/film (NFG) systems and NPs/graphene gap/NPs (NNG) structures, have been proposed. For example, Li et al. have applied monolayer graphene as the nanospacer into Ag film-AgNPs coupling system and obtained SERS spectra with high relative intensities [14]. And the NFG system of CuNPs directly deposited on a chemical vapor deposition (CVD) grown graphene/copper film have been also demonstrated by them [15]. Similarly, Xiang et al. have prepared AuNPs/graphene/copper foil hybrid configuration as an SERS substrate [16]. Kim et al. have demonstrated single nanowire on graphene, which could be used as an efficient, reproducible, and stable SERS-active platform [17]. Zhan et al. fabricated AuNPs/Graphene/AuNPs sandwiched structures to reach ultrahigh SERS factor [18]. And Lee et al. investigated a rippled structure containing multilayer graphene as a nano-spacer for improving plasmonic coupling [19]. Such NFG and NNG platforms facilitate the studies of hot spots in SERS substrates. In addition to hot spots from the conventional interparticle and particle-film nanogaps, some relatively complex topography, Ag cubes [20], Au triangular nanoarrays [21], nano-porous [22] and nano-polyhedrons [23] likewise, have been fabricated interestingly to optimize the SERS performance and possessed higher SERS activity compared with the conventional interparticle and particle-film nanogaps. However, few works aimed at the combining of the graphene and complex topography have been reported.

In this work, we fabricated AgNPs/bilayer graphene/Au nanonet composite structure for SERS substrate with a simple method. In such a configuration, Au nanonet with polyporous and multilateral structure makes the hot spots dense. Using graphene as ultra-narrow nano-gap, the strong coupling between AgNPs and Au nanonet is obtained, similarly, this structure simultaneously generates combination of numerous tip-enhanced Raman scattering (TERS). In addition, the graphene can also provide the enhancement based on CM. Due to producing the extremely excellent SERS performance, the SERS signals of Rhodamine 6G (R6G) and crystal violet (CV) was respectively detected at very low concentration of 10^{-13} M and 10^{-12} M. To demonstrate the advantage of this configuration, the electric field distribution was modeled by using commercial COMSOL software. Malachite green (MG), as a harmful carcinogen, will render malformation and mutagenic side effects. However, it has been frequently and illegally abused in aquaculture to avoid the rot of fish. Therefore, many countries have taken actions to prohibit the abuse of the MG in marine products. Now, it is urgent need to develop a highly sensitive method for the MG molecules detection. We achieved the low limit (as low as the US Food and Drug Administration (US FDA) and European Commission standard: 0.001 (Collette, 2006) and 0.002 mg kg^{-1} (Commission Decision, 2004/25/EC) approximately are 10^{-9} M) of detection of the MG that was detected at very low concentration of 10^{-12} M based on AgNPs/bilayer graphene/Au nanonet substrate. There is great potential for our work to develop a facile strategy for SERS detection of chemical molecule in food safety field.

2. Material and methods

2.1. Materials

For preparing AgNPs/bilayer graphene/Au nanonet substrate, the raw material of Au nanonet and AgNPs respectively is Au wire (99.99%, 0.1 mm diameter) and Ag wire (99.99%, 0.1 mm diameter), which were purchased from Sinopharm chemical reagent Co., Ltd. The Cu foil (0.025 mm thickness) for the growing graphene was purchased from Alfa Aesar (China) chemicals Co., Ltd. Next, for demonstrating SERS activity, R6G (AR, 5 g) was purchased from MaiKun chemical. CV (AR, 100 g) was purchased from Yuanye biotechnology Co., Ltd (Shanghai). MG (AR, 25 g) was purchased from Aladdin industrial corporation (Shanghai). The polymethyl methacrylate (PMMA) was purchased from Aladdin chemistry Co., Ltd.

2.2. The fabrication of AgNPs/bilayer graphene/Au nanonet composite structure

All the rectangle transparent SiO_2 substrates used in the experiments were pretreated to remove oil stains according to our previous report [24]. After the basic assignment, the uniform Au thin film was deposited on the substrate using physical vapor deposition (PVD). The thickness of Au film will be demonstrated in results and discussion section. To transfer the graphene on the Au film, PMMA/acetone solution (0.0750 g/100 mL), which is a support as protective layer, was coated on graphene on Cu foil. And then the derived sample was immersed into $FeCl_3$ solution (~1 M) to absolutely etch Cu foil. After that the remaining PMMA/graphene layer was carefully transferred into DI water for 5 times to remove the residual etching solution. Next, PMMA/graphene layer in DI water was gently fished up by the obtained Au film and was blown dry under nitrogen atmosphere and was baked under 130 °C in order to make PMMA/graphene layer closely paste on the surface of metal thin film. After that the sample was put into 100 mL acetone solution, which was heated to 80 °C for 10 times to completely remove the coating layer (PMMA). Based on such a process, the perfect bilayer graphene was obtained and an ultra-narrow gap (0.68 nm) was built. After this, uniform Ag film (the raw materials of 0.0015 g were used) was evaporated on the surface of graphene using PVD. Finally, the Ag film/bilayer graphene/Au film on SiO_2 respectively was put into the tube furnace to anneal at 400 °C for 5, 10, and 15 min in the 40 sccm Ar environment. After the process of annealing, the Ag film and Au film were dewetted into the AgNPs and Au nanonet. The above samples respectively are labeled as 1#, 2#, and 3# substrate, where the pressure is 8.50 Pa in quartz tube. Through the above steps, the composite SERS substrate was prepared with a simple method, where no expensive equipment was involved.

2.3. Apparatus and characterization

To clearly observe the surface morphology of the above mentioned samples, the SERS substrates were characterized by atomic force microscope (AFM Bruker Multimode 8) and scanning electron microscope (SEM ZEISS Gemini SUPRA55) apparatus. SERS spectra were detected by Raman spectrometer (Horiba HR Evolution 800) with laser wavelength of 532 nm with the laser excitation energy of 0.48 mW, and the spot size of 1 μm, and the diffraction grid of 1800 gr/mm. A 50 × objective with the spatial resolution of 400 nm and the integration time of 8 s were used throughout the experiment.

3. Results and discussion

3.1. Theoretical calculation for carefully selecting metal materials to form optimum configuration

Because of the strong LSPR effect from AgNPs and AuNPs, they have been the famous stars for realizing ideal SERS performance. To obtain the optimum EM, the different couplings of AgNPs and AgNPs, AuNPs and AuNPs, AgNPs and AuNPs were structured to calculate the local electric field enhancement in theory using COMSOL (RF module) Multiphysics software. The diameters of all NPs were set as 36 nm, which will be demonstrated in the following experimental results. And the ultra-small nanogaps between the adjacent NPs was set as 0.68 nm, which is approximately equal to the