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Constructing sub-10-nm gaps in graphene-metal hybrid system for advanced surface-enhanced Raman scattering detection

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ABSTRACT

We prepared a three-dimensional (3D) hybrid structure by assembling dense gold nanoparticles (Au NPs) on graphene supported on electron beam lithography-fabricated silver nanodisk arrays (Ag NDAs). Using the strategy of modulating the structure parameters via EBL system to sufficiently narrow the distances between adjacent disks, we successfully constructed sub-10-nm gaps between the horizontally patterned Ag NDs. Moreover, uniform nanometer-scale graphene gaps were obtained between Au NPs and Ag NDAs. Finite element numerical simulations revealed that the multi-dimensional plasmonic couplings in the 3D Au NP-graphene-Ag NDA system led to an electric field enhancement up to 112 times in graphene defined gaps. As demonstrated by our SERS measurements, the well-designed and fabricated 3D Au NP-graphene-Ag NDA hybrid structure exhibits 3200-fold enhancement of the Raman response of graphene, and sensitive SERS detection with a limit of 0.1 pM for crystal violet molecules, which can be attributed to the extremely strong electric field enhancement and chemical enhancement of graphene. This work represents a step towards high-sensitivity and strong-reproducibility SERS substrate fabrication, and opens a new avenue for rationally designing graphene-plasmonic hybrid structures for SERS sensing.

1. Introduction

Surface-enhanced Raman scattering (SERS), capable of providing high-resolution structure fingerprints and achieving single-molecule detection, has stimulated widespread interest ranging from analytical chemistry to medicine, food safety as well as environmental regulation [1–5]. This spectacular signal enhancement is mainly attributed to a confined electromagnetic (EM) field arising from the excitation of surface plasmon resonances, which is localized in the interparticle gaps, and over the sharp edges, corners and tips of metal nanoparticles (NPs), e.g., EM "hot spots" [6–8]. In particular, there is a consensus that the Raman signal of molecules in close proximity to the sub-10-nm gap formed EM hot spots can be greatly amplified, leading to an enhancement factor (EF) of 10^8 or more [9,10]. As a result, SERS substrates possessing small gaps with an excellent homogeneity will benefit to the sensitive and reproducible SERS sensing and detection. For engineering small interparticle gaps, the utilization of electron beam lithography (EBL) technology has been proved to be an efficient method to fabricate ordered structure arrays, which enables the precise control of the size and shape of NPs [11,12]. Given the technical restriction (e.g., the proximity effect in the electron-beam exposure process) [13], however, it remains a great challenge to prepare periodic nanoarrays containing high-density gaps in 10-nm range or below. Moreover, the effective adsorption and selective position for the analytes of interest on the hot spots for maximal SERS sensitivity can not be achieved easily [14]. Even worse, the molecules dropping into the bottom of interparticle spaces hardly contribute to the observable SERS signal enhancement, which inevitably weaken the sensing sensitivity and restrict

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the practical applications. On the other hand, chemical enhancement, originating from the charge transfer between molecules and substrates, can induce a SERS signal enhancement of ~10–100 [15].

In quest to improve the SERS substrate sensing sensitivity and reliability, both materials and structures should be optimized for the creation of high-density and uniform gaps. Graphene is a single layer of carbon atoms arranged in a two-dimensional hexagonal lattice. Since the discovered Raman activity, graphene has been considered as a pioneering sensing material for its atomic thickness, chemical stability and biological compatibility [16,17]. Inspiringly, the hybrid systems of graphene and metal NPs have been explored to improve the SERS sensitivity for additional chemical enhancement [18]. In the previous studies, graphene-metal NPs bilayers, including assembling metal NPs on graphene and covering graphene on metal NPs, have been reported to improve the SERS sensitivity. As a demonstration, ~10-fold stronger Raman signals have been obtained for the system of gold (Au) NPs covered with monolayer graphene (1LG) when compared with bare Au NPs [19,20]. Recently, configurations of graphene oxide (GO) (or reduced graphene oxide, RGO) sandwiched between metal NPs have been prepared by chemically synthesizing metal NPs and GO/RGO in solution and assembling them on the substrates [21,22]. In these structures, the electric fields have been dramatically amplified due to the generation of nanometer scale graphene gaps. Nevertheless, the unordered dispersions of the wet-chemical approach-synthesized metal NPs and GO/RGO on planar substrates generally lead to the stacking of metal NPs and GO/RGO, and oxidation of metal and RGO [23], thus suppressing the reliability and stability of SERS signals. It has been demonstrated that graphene can be considered as a dielectric when it was sandwiched between two layers of metals NPs [24]. Graphene embedded metal NPs structure has been prepared by sandwiching graphene between two layers of anneal-formed Au NPs [25]. However, the EM hot spots exhibit an out-of-order distribution resulting from the irregular shapes and random location sites of Au NPs at the bottom layer, thus limiting the SERS signal reproducibility. If secondary deposition and assembly of metal NPs can be grafted on an ordered structure, EM hot spots with a uniform distribution will be formed, thus SERS substrates with high uniformity and sensitivity could be expected.

Herein, we present an effective approach to fabricate highly uniform and ordered 3D SERS substrate with single layer graphene sandwiched between Au NPs and EBL-fabricated silver nanodisk arrays (Ag NDAs). The structure parameters of the bottom Ag NDAs have been optimized to decrease the interdisk spaces. Importantly, the precise control of the size written by electron beam enables the uniform fabrication of NDAs with an interparticle space in the range of 10 nm or below. Finite element numerical simulations reveal that the multi-dimensional plasmonic couplings of the 3D platform, including Au NP-Au NP, Au NP-Ag ND, Ag ND-Ag ND couplings, allow the hybrid structure to exhibit extremely strong electric field enhancement. Enabled by the as-prepared 3D Au NP-1LG-Ag NDA hybrid structure, 3200-fold enhancement of the Raman response of graphene, and high-sensitivity SERS detection for crystal violet (CV) molecules with good uniformity and reliability have been achieved. This work demonstrates promising potentials for the fabrication of SERS substrates with high sensitivity and good reliability.

2. Experimental

2.1. Fabrication of the Au NP-1LG-Ag NDA structure

The core concept of the Au NP-1LG-Ag NDA structure fabrication involves the writing of a pattern by EBL, graphene transfer, and metal film deposition and annealing processes. Fig. 1 shows the fabrication procedure for the Au NP-1LG-Ag NDA structure. In a standard preparation process, a thin layer of poly(methyl methacrylate) (PMMA) (~260 nm thickness) was spin-coated on a silicon (Si) wafer at 3500 rpm for 60 s and backed at 180 °C for 90s on a hot plate. A NDA pattern was written using an EBL system (JEOL JBX-6300FS) with an area dosage of 800 μC/cm^2 and a current of 100 pA. After the exposure, the sample was immersed into a solution of methyl isobutyl ketone (MIBK) and isopropanol (IPA) in a 1:3 mixture ratio for 60 s to process developing, and rinsed in IPA for 60 s [26], followed with a gentle N^2 blow, thus forming a PMMA NDA pattern (step 1). A 5 nm-thick Cr adhesion layer and 50 nm-thick Ag layer were deposited sequentially onto the sample surface at rates of 0.5 Å/s under the pressure of about 10^{-4} mbar by magnetic sputtering (step 2). And then the sample was immersed into acetone to process lift-off to form Ag-Gr NDAs structure (step 3). For convenience, we call it Ag NDAs. Monolayer graphene films grown on copper (Cu) foils by chemical vapor deposition were transferred onto the Ag NDAs for constructing 1LG-Ag NDA structure (step 4). In a standard transfer process, a PMMA layer (~300 nm thickness) was spin-coated onto the surface of monolayer graphene films on Cu foils and dried on a hot plate at 150 °C [27,28]. The PMMA-graphene-Cu foil was placed in ammonium persulfate (0.07 g/ml) to etch away the Cu foils, washed with deionized (DI) water, and then transferred onto the surface of Ag NDAs. Before the following operations, a thermal treatment could help the graphene films fit well with Ag NDAs. The sample was immersed in acetone to dissolve PMMA for the generation of 1LG-Ag NDA structure. Finally, a thin layer of 6 nm-thick Au film was deposited slowly onto the surface of as-prepared 1LG-Ag NDA at a rate of 0.1 Å/s by magnetic sputtering and annealed in Ar at 300 °C for 60 min with a heating rate of 5 °C/min, thereby achieving 3D Au NP-graphene-Ag NDA hybrid structure (step 5).

2.2. Characterization

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to characterize the morphologies of the samples. CV solutions with different concentrations were obtained by dissolving the solid powders and diluting using ethanol. For measuring the Raman signals of CV molecules, a 10 μL droplet was dispersed on the substrate prepared and dried in air. Raman spectra were measured utilizing Renishaw inVia Raman Microscope with an excitation wavelength of 532 nm and 1800 line/mm grating. The laser power was maintained at 5 mW for measuring graphene and 0.5 mW for measuring dye molecules to protect the samples from possible heating and photo-induced damages. A × 50 objective was used and the laser spot was ~1 μm^2. The integration time was 1 s.

2.3. Finite element method simulations

The software package “Comsol Multiphysics”, which relies on finite element method to solve Maxwell's equations, has been used in the simulations [29–31]. For the simulation configuration, in the vertical direction, perfectly-matched-layers were used for eliminating the undesired reflections from boundaries, and in the horizontal directions, periodic boundary conditions were set for simulating a single unite cell and thereby saving simulation time [21,26]. The incident wavelength was set to be 532 nm with the electric field polarized along the y-axis. The optical parameters of Au and Ag were set using Drude model [32], the dielectric constant of graphene was calculated using the formula $n = 3 + c_1(\lambda/3)i$ ($c_1 = 5.446\ \mu m^{-1}$ and λ was the wavelength) [33] and the refractive index of Si was 3.66. Convergence mesh analysis was applied to reach stationary results.