

Research Article

Highly Stable Surface-Enhanced Raman Spectroscopy Substrates Using Few-Layer Graphene on Silver Nanoparticles

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Graphene can be effectively applied as an ultrathin barrier for fluids, gases, and atoms based on its excellent impermeability. In this work, few-layer graphene was encapsulated on silver (Ag) nanoparticles for the fabrication of highly stable surface-enhanced Raman scattering (SERS) substrates, which has strong resistance to oxidation of the Ag nanoparticles. The few-layer graphene can be successfully grown on the surface of the Ag nanoparticles through a simple heating process. To prevent the agglomeration of the Ag nanoparticles in the fabrication process, poly(methyl methacrylate) (PMMA) layers were used as a solid carbon source instead of methane (CH_4) gas generally used as a carbon source for the synthesis of graphene. X-ray diffraction (XRD) spectra of the few-layer graphene-encapsulated Ag nanoparticles indicate that the few-layer graphene can protect the Ag nanoparticles from surface oxidation after intensive annealing processes in ambient conditions, giving the highly stable SERS substrates. The Raman spectra of Rhodamine 6G (R6G) deposited on the stable SERS substrates exhibit maintenance of the Raman signal intensity despite the annealing process in air. The facile approach to fabricate the few-layer graphene-encapsulated Ag nanoparticles can be effectively useful for various applications in chemical and biological sensors by providing the highly stable SERS substrates.

1. Introduction

Surface-enhanced Raman scattering (SERS), which is a promising spectroscopic technique for ultrasensitive and nondestructive detection of subtle analysis at low concentration, has attracted a huge amount of interest for various applications such as chemical and biosensors, forensic analysis, threat detection, diagnostics, and food safety [1–6]. To ensure efficient SERS platform, several roughened metal nanostructures including silver (Ag) and gold (Au) have been generally investigated since the metal surfaces can induce a dramatic enhancement of Raman scattering signal through light-excited localized surface plasmonic resonance [7, 8]. Although the SERS based on the metal nanostructure substrates has been widely developed due to its outstanding performances, there are some challenges such as instability of the metal substrate to oxidation or sulfidation (especially in the case of the Ag-based substrate) and the low reproducibility of the Raman signal arising from photoinduced damage [9, 10]. In particular, poor chemical stability of Ag-based

SERS substrate against oxidation under ambient condition can give rise to a significant reduction in intensity of the Raman signal due to morphological and chemical changes of the metal nanostructures. To overcome the limitation related to the chemical instability of the substrate, protecting layers for the metal SERS substrate such as TiO_2 , SiO_2 , Al_2O_3 , and amorphous carbon have been explored [11–14]. However, since the thick protecting layers without any pinhole generally disrupt the interaction between the metal nanostructure of the substrate and molecules, the SERS intensity can be significantly reduced due to the impaired surface plasmon which is a near-field interaction by nature.

Graphene, a carbon-based material fully packed into a honeycomb lattice, has been extensively investigated due to its outstanding properties such as excellent mechanical, optical, electrical, and chemical properties [15, 16]. Based on the superb chemical inertness and surface plasmonic property, a monolayer graphene grown by chemical vapor deposition (CVD) process or chemically exfoliated graphene oxide (GO) has been demonstrated as an ultrathin protecting

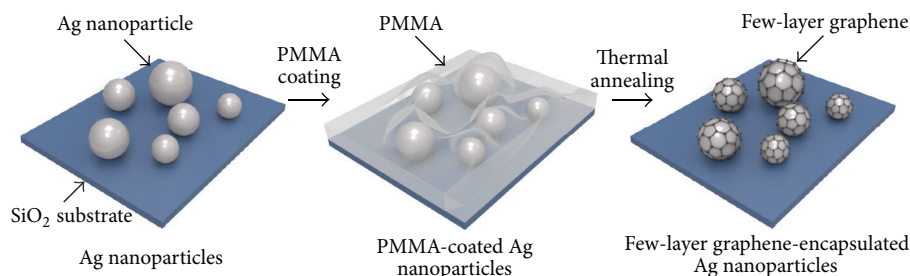


FIGURE 1: Fabrication process of few-layer graphene-encapsulated Ag nanoparticles using a solid carbon source (PMMA).

layer of Ag-based SERS substrates [7, 17]. The graphene or GO can act as an effective protective shell with high performance for SERS; nevertheless, it is difficult to achieve a simple process and scalability for large-scale synthesis due to the limitations from an additional transfer process of graphene or an electrostatic assembly of GO. Recently, Liu et al. demonstrated an efficient graphene shell directly grown by a CVD process without any transfer process for the protection of metal nanoparticles from oxidation [18]. The graphene-encapsulated metal substrates for SERS can be useful to protect the metal substrates from oxidation and obtain high performances for SERS; however, it is difficult to control size and assembly of the metal nanoparticles which is important to achieve high sensitivity and reproducibility due to the growth process of graphene under high temperature.

In this research, we describe a facile process to directly grow the few-layer graphene on Ag nanoparticles using a solid phase carbon source of poly(methyl methacrylate) (PMMA). The few-layered graphene could be directly synthesized on Ag nanoparticles without the agglomeration of the nanoparticles using the solid carbon source, which was confirmed from the Raman analysis. The high-resolution transmission electron microscope (HR-TEM) images also verified the synthesis of the few-layer graphene on the surface of Ag nanoparticles. The few-layer graphene-encapsulated Ag nanoparticles exhibited excellent long-term stability against oxidation and high performance as a SERS substrate.

2. Experiment Section

2.1. Synthesis of Ag Nanoparticles for SERS Substrates. A mixed solution composed of 1.5 mL of 94 mM Ag nitrate (AgNO₃) solution with 1.5 mL of 147 mM polyvinylpyrrolidone (PVP) solution was added to 5 mL of ethylene glycol previously heated for 1 h at 152°C. After the mixed solution was stirred for 30 minutes, it was cooled to room temperature and centrifuged at 3,500 rpm for 20 min to remove the ethylene glycol. Then, the obtained Ag nanoparticles were diluted with methanol and centrifuged at the same conditions several times to remove PVP residues. The synthesized Ag nanoparticles were dispersed in 10 mL of deionized water (DI water).

2.2. Growth of the Few-Layer Graphene on Ag Nanoparticles. 5 mL of the Ag nanoparticle solution in DI water (about 2 wt%) was mixed with 10 mL of PMMA solution (2 wt%)

dissolved in Anisole and the mixed solution was stirred using a magnetic bar. After 12 h, the mixed solution was drop-cast on cleaned SiO₂ substrate and heated at 110°C for 10 min. For the growth of the few-layer graphene, 20 sccm of H₂ and 70 sccm of Ar gases were introduced to a CVD furnace which includes the sample and heated at 800°C. After 15 min, the sample was cooled down to room temperature under ambient condition.

2.3. SERS Measurements. Rhodamine 6G (R6G) was used as probing molecules for SERS measurement of the few-layer graphene-encapsulated Ag nanoparticles. The prepared SERS substrates were immersed in R6G solution (10⁻⁶ M) dissolved in DI water for 12 h and then dried under nitrogen flow. A HORIBA Lab Ram ARAMIS Raman spectrometer was used for the SERS measurement. Ar⁺ laser (514 nm) and He-Ne laser (633 nm) were employed as a light source and laser power of 20 μW was used for 1 s in order to characterize the few-layer graphene on Ag nanoparticles and R6G molecules.

2.4. Characterization. Surface morphologies of the sample were characterized using a JEOL JSM-7001F field emission scanning electron microscope (FE-SEM) and a JEOL JEM-2010 HR-TEM. X-ray diffraction (XRD) spectrum was measured with Rigaku D/MAX-2500H X-ray diffraction spectroscopy.

3. Results and Discussion

Figure 1 shows a schematic illustration of the fabrication process of the few-layer graphene on Ag nanoparticles using a solid carbon source. Ag nanoparticles were covered with PMMA as the solid carbon source on SiO₂ substrates and then the few-layer graphene could be grown on the surface of the Ag nanoparticles using high temperature in Ar and H₂ atmosphere. During the annealing process, the PMMA layer could be converted to a-C layer on the Ag nanoparticles through a pyrolysis process at increased temperature over 400°C [19]. Then, the a-C layer which prevents the agglomeration of the Ag nanoparticle could be converted to the few-layer graphene with the help of catalytic effect of Ag at high temperature around 800°C [20].

The Ag nanoparticles used in this research were synthesized by the polyol process. Most Ag ions in the ethylene glycol used as a reduction agent as well as a solvent for the Ag ions were reduced into twinned or multiply twinned

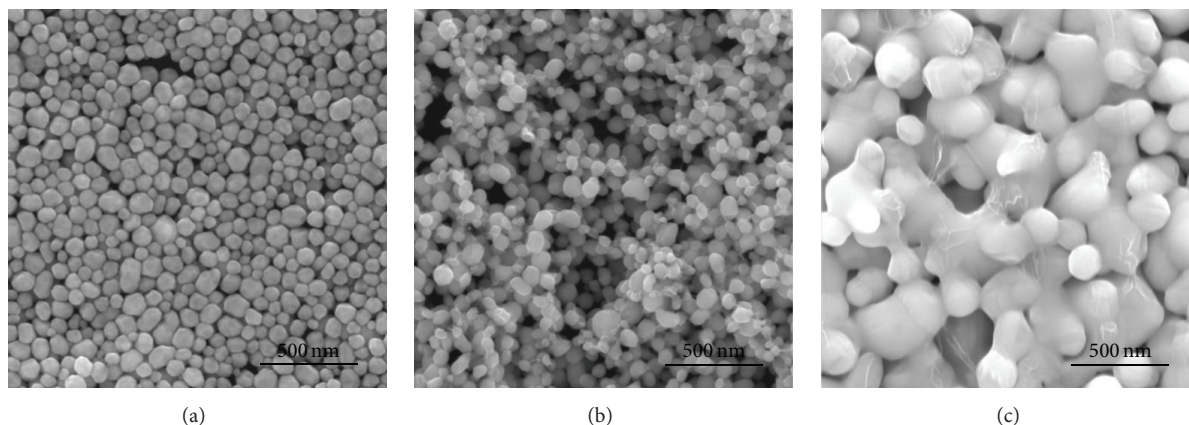


FIGURE 2: Typical SEM image showing (a) the as-prepared Ag nanoparticles on SiO_2 substrates, (b) few-layer graphene-encapsulated Ag nanoparticles, and (c) the agglomerated Ag nanoparticles after annealing process using a gas-phase carbon source (CH_4 gas).

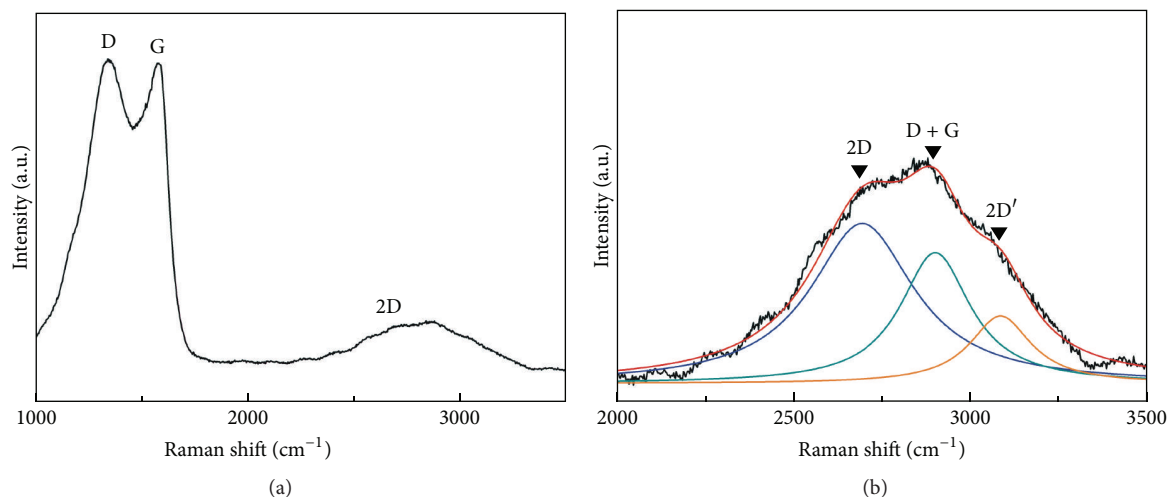


FIGURE 3: (a) Raman spectra of the few-layer graphene-encapsulated Ag nanoparticles and (b) the detailed analysis of 2D peak fitted using Lorentzian profiles.

particles that have $\{111\}$ facets with the lowest energy through annealing process. Through addition of PVP as a capping agent, Ag nanoparticles with a spherical shape could be successfully synthesized from the Ag multiply twinned particles. Figure 2(a) exhibits an SEM image of the prepared Ag nanoparticles with an average diameter of 82 nm. When the synthesis process of the few-layer graphene was conducted at 800°C using the solid carbon source (PMMA), the Ag nanoparticles showed no significant morphological changes as shown in Figure 2(b). The Ag nanoparticles could be protected from the high temperature by the solid carbon source and the formed carbon shells during the annealing procedure [19]. However, in the case that methane gas (CH_4) generally used for the synthesis of graphene using CVD process was employed, the Ag nanoparticles were highly agglomerated, forming clustered structures (Figure 2(c)). The agglomeration of the Ag nanoparticles during the annealing process with the gas source can be attributed to the high temperature (800°C) which is needed to synthesize the graphene. Although the melting temperature of Ag is well known to

be 961.8°C , the melting temperature of Ag nanoparticles can be decreased due to the increased vapor pressure of the Ag surface atoms in the nanoscale dimension, inducing the agglomeration of the Ag nanoparticles to minimize the surface energy [21].

To verify the synthesis of graphene layers on the surface of the Ag nanoparticles, structural characteristics of the graphene layers were confirmed by Raman spectroscopy. In Figure 3(a), the graph provides the Raman spectra of the sample, including superpositioned D and G peaks near 1360 cm^{-1} and 1590 cm^{-1} , respectively, and a broad peak at $2300\text{--}3200\text{ cm}^{-1}$. The high intensity of the D peak means the defective structure of the graphene layer on the Ag nanoparticle, resulting from very small domains of the graphene due to the high curvature of the Ag nanoparticle surfaces. The high curvature can also induce a considerable stress on the lattice of the graphene. In addition, the larger size ($1\text{ }\mu\text{m}$) of the laser beam in Raman spectroscopy than the Ag nanoparticles can result in the increase of the D peak since the laser beam would include many spherical graphenes at the same time [19]. The

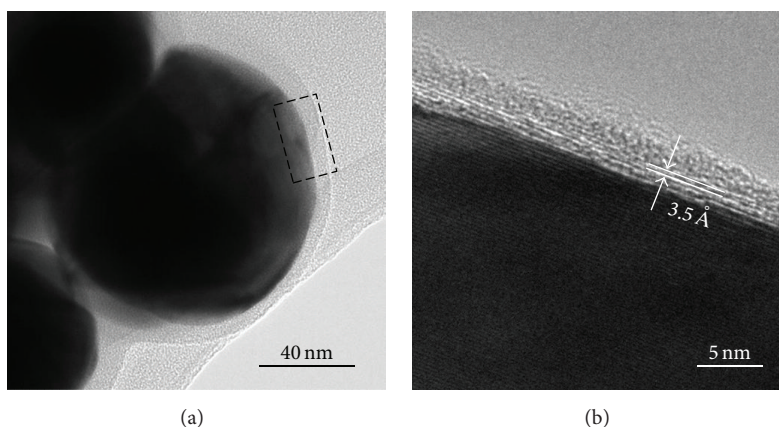


FIGURE 4: (a) A typical TEM image of the few-layer graphene-encapsulated Ag nanoparticles and (b) the high-resolution TEM image of (a) showing few graphene layers with about 3.5 nm of thickness on the Ag nanoparticle.

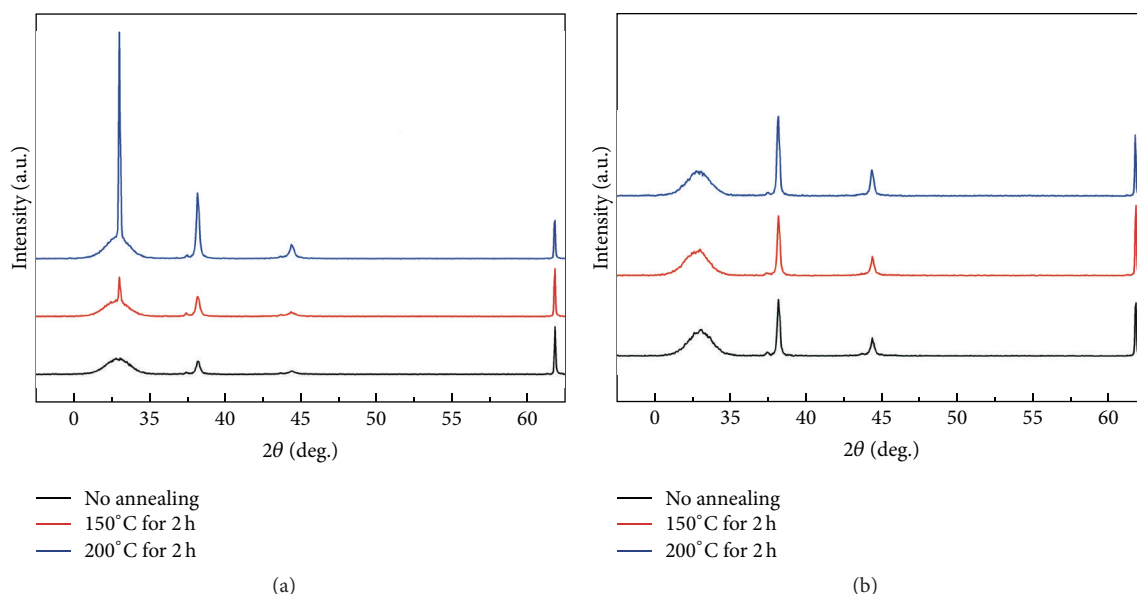


FIGURE 5: XRD spectra of (a) Ag nanoparticles without any protective layer and (b) few-layer graphene-encapsulated Ag nanoparticles before and after annealing process.

broad 2D peak near $2300\text{--}3200\text{ cm}^{-1}$ may be attributed to the nonplanar structure of the graphene layer on the Ag nanoparticles. Figure 3(b) shows the detailed analysis of the 2D peak using Lorentzian profiles, indicating that the D peak is composed of 2D (2694 cm^{-1}), D + G (2901 cm^{-1}), and $2\text{D}'$ peaks (3807 cm^{-1}). In particular, the generation of the D + G and $2\text{D}'$ peaks can be characterized by the strained structure of nonplanar graphene layer on the Ag nanoparticles [22, 23]. Figures 4(a) and 4(b) provide TEM images of the graphene shell covering the Ag nanoparticles. In Figure 4(b), the HR-TEM shows clearly that the distance between coating layers was about 0.35 nm which is consistent with the interlayer distance of graphite [24], suggesting the growth of the few-layer graphene on the surface of the Ag nanoparticles.

Since graphene is impermeable to fluids, molecules, atoms, and even standard gases including helium [25], the

few-layer graphene grown on the surface of the Ag nanoparticles can act as an excellent protective layer against the oxidation of the Ag nanoparticles which can significantly reduce the SERS performance, ensuring the stability of the Ag-based SERS substrates. To evaluate the stability of the few-layer graphene-encapsulated Ag nanoparticles against oxidation, the samples were annealed at 150°C and 200°C for 2 h under ambient conditions and the XRD measurements were performed. Figure 5(a) shows the XRD spectra of the SERS substrates composed of Ag nanoparticles without any protective layer. Several peaks at 37.5° , 43.7° , and 64.1° in the spectra are characterized by (111), (200), and (220) planes of the face-centered cubic silver [17]. When the samples were heated under ambient conditions, a peak at 32.7° which indicates the formation of the (111) crystal plane of Ag_2O (JCPDS number 41-1104) additionally appeared in the graph.

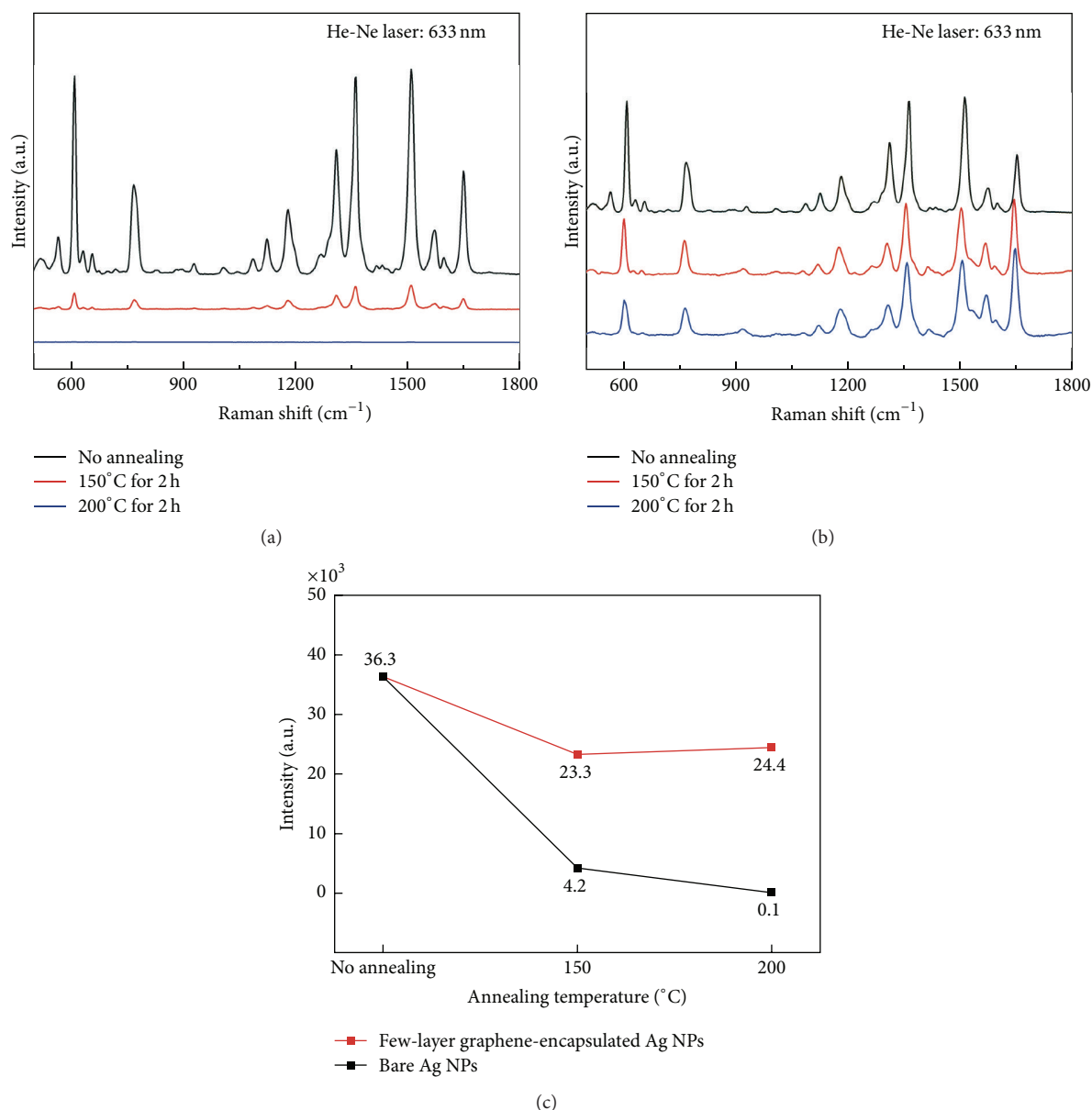


FIGURE 6: Raman spectra obtained using R6G as a probing molecule. SERS spectra of R6G deposited (a) on the Ag nanoparticles without any protection for oxidation and (b) on the few-layer graphene-encapsulated Ag nanoparticles were measured. The measurement was performed before and after annealing process in ambient conditions and He-Ne laser (633 nm) was employed for the measurement. (c) Quantitative analysis of the change of the Raman intensity at 1363 cm⁻¹ according to the annealing process in the case where the bare Ag nanoparticles and the few-layer graphene-encapsulated Ag nanoparticles were used as SERS substrates.

It can be known that the intensity of the peak is considerably increased as the annealing temperature is increased, providing the evidence of oxidation of the Ag nanoparticles. On the contrary, in the case of the few-layer graphene-encapsulated SERS substrates, the peak related to the oxidation of Ag could not be detected despite the intensive annealing process in air as described in Figure 5(b). These results indicate that the few-layer graphene covering the Ag nanoparticles acts as an effective barrier for the aerobic oxygen and provides the ability to suppress oxidation of the Ag nanoparticles to the SERS substrates.

To demonstrate the stability of the few-layer graphene-encapsulated Ag nanoparticles for SERS measurements, Raman spectra of R6G, a probing molecule, on the Ag nanoparticles with and without few-layer graphene were measured. In Figure 6(a), the spectra exhibit the SERS spectra of the R6G with the concentration of 10⁻⁶ M on the Ag nanoparticles without any protective layer. Clear peaks described in the graph can be characterized by C-C-C ring in-plane bending (612 cm⁻¹), C-H out-of-plane bending (773 cm⁻¹), aromatic C-H bending (1183 cm⁻¹), C-O-C stretching (1312 cm⁻¹), and aromatic C-C stretching

(1650, 1575, 1511, and 1363 cm^{-1}) [26]. Although the main Raman peaks of R6G on the Ag nanoparticles were clear, their intensities were drastically decreased according to the increase of the annealing temperature in air. However, Figure 6(b) shows that the Raman intensities of R6G on the few-layer graphene-encapsulated Ag nanoparticles were maintained in spite of the annealing process in ambient conditions. As quantitatively analyzed in Figure 6(c), when the bare Ag nanoparticles were used as the SERS substrates, the Raman intensity of the particular peak (1363 cm^{-1}) of R6G remarkably decreased by a factor of 0.003 (36304 to 113) under the extensive annealing process in air. However, there was no considerable decrease in the Raman intensity of the same peak (36304 to 24436) despite the annealing process in the case that the few-layer graphene-encapsulated Ag nanoparticles were used, which indicates that the few-layer graphene effectively prevents the oxidation of the Ag nanoparticles during the annealing process. Regarding the reproducibility of the few-layer graphene-encapsulated Ag nanoparticles as the SERS substrate, enhancement factor (EF), calculated by intensity ratio (I/I_0) between the Raman peak at 1183 cm^{-1} of the R6G on the few-layer graphene-encapsulated Ag nanoparticles (I) and bare silicon substrates (I_0), for three samples was measured to be 682, 902, and 697 without considerable difference, indicating that the SERS substrates provide comparable reproducibility. From these results, it can be expected that the few-layer graphene can be effectively used to fabricate highly stable SERS substrates, which is sufficiently resistant to oxidation of the Ag nanoparticles for various bioanalysis and biosensor applications.

4. Conclusions

In summary, a SERS substrate with high performance and stability against oxidation was prepared by encapsulating few-layer graphene on surfaces of Ag nanoparticles. The few-layer graphene was directly grown on as-prepared Ag nanoparticles through a simple annealing process with a solid carbon source. The few-layer graphene effectively protected the Ag nanoparticles from oxidation and suppressed the decline of the SERS performance of the Ag nanoparticles-based substrates during annealing process in ambient conditions. The formation of the few-layer graphene was verified by measuring the Raman spectra and HR-TEM images and the stability of the few-layer graphene-encapsulated Ag nanoparticles against oxidation was demonstrated through the XRD and SERS measurements. The highly stable SERS substrates based on few-layer graphene in this work are expected to be useful for many practical applications in chemical and biological sensor.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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