

Research Article

Highly Sensitive Surface Enhanced Raman Spectroscopy from Ag Nanoparticles Decorated Graphene Sheet

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Surface enhanced Raman spectroscopy (SERS) is a powerful analytical technique and has been most intensively studied. In this work, electroless deposition is proposed for Ag nanoparticles (NPs) decorated on chemical vapor deposition (CVD) growth graphene sheets (GS) to create hybrid SERS substrate. From three aspects of size distribution, morphology, and coverage, Ag NPs controllable decoration on GS and SERS enhancement factors of the hybrid SERS substrate is investigated. 200–300 times enhanced SERS intensities are detected from the Ag NPs on GS hybrid as compared to pure GS. Controllable decoration is crucial for improving SERS enhancement factors β_{EF} , because β_{EF} from quasi cubic Ag NPs on GS is 6.53 times stronger than that from spheric one; 1.6 times β_{EF} is detected while the Ag NPs size distribution is reduced to half, and when the coverage is doubled, β_{EF} is nearly doubled. This controllable Ag NPs/GS hybrid is capable of serving as a high performance SERS substrate for efficient chemical and biological sensing applications.

1. Introduction

Due to its high sensitivity, low background fluorescence noise, capability of single molecular recognition, and nondestructive testing of samples, surface enhanced Raman scattering (SERS) technique, as an important detection technology, is widely applied in chemical sensing [1–3], photonics [4], catalysis [5], ultrasensitive biosensors [6, 7], and many other areas [8, 9]. In the past, rough metals surface and metal nanostructure of SERS substrate have attracted many attentions because of the huge enhancement factors (EF) β_{EF} they induced through the electromagnetic mechanism effect [10, 11]. Rough-surface treatment for metal electrode and noble metal sol nanoparticles (NPs) are commonly used in SERS substrate process [5, 12–15], because SERS β_{EF} depends largely on the type and morphology of the metal. However, these approaches cannot accurately control the roughness and uniformity of the SERS substrate or the size distribution, morphology, and coverage of the metal NPs and result in consequent unstable and no reproducible SERS analysis and lower

β_{EF} . Therefore, it is necessary to explore a SERS substrate with high stability and controllable uniformity or roughness.

Graphene has shown to be emerging material of SERS substrate due to its ability to generate strong chemical enhancement [16]. A new SERS substrate, forming by introducing Ag NPs to graphene sheets (GS) that take advantage of both traditional metallic substrate and graphene substrate, brings a new insight into practical applications [1, 4–6]. SERS signals arising from graphene/Ag hybrid substrate are also shown to be higher compared to each of them [5–13, 17]. SERS substrate decorated with silver nanostructure has attracted considerable attention [6, 11–14]. Tzounis et al. [18] enhanced SERS intensities by depositing Ag NPs with controllable and uniform size onto the surface of silica spheres. Zhang et al. [13] obtained SERS β_{EF} up to 7 for G peak when 30 nm Ag NPs covered by graphene with ion beam assisted deposition and annealed system. Sidorov et al. [19] showed an SERS β_{EF} of about 150-fold by decorating graphene with 30–40 nm Ag NPs and ~50 nm Ag nanorods/nanowires (NRs/NWs).

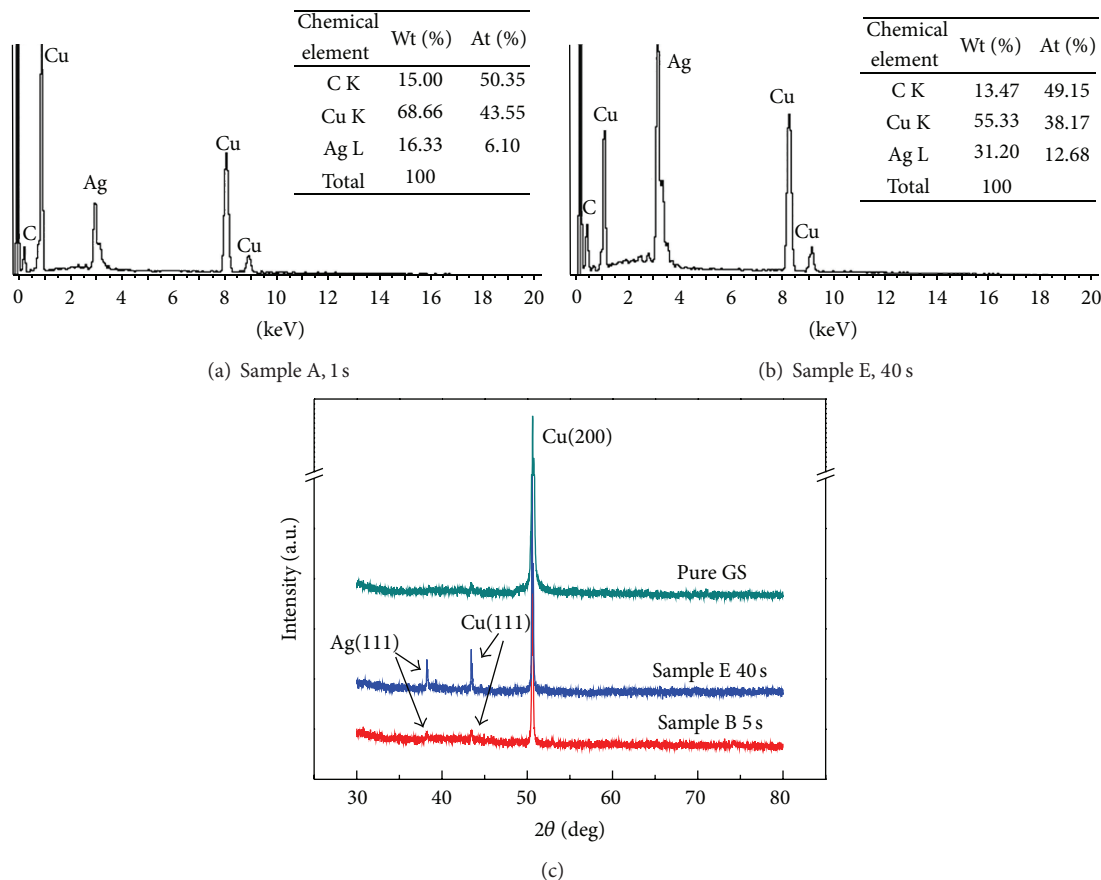


FIGURE 1: Normalized EDS spectrum of (a) sample A and (b) sample E and (c) XRD patterns of Ag NPs on GS hybrid samples.

Fan et al. [9] revealed that the single-particle SERS β_{EF} for Ag nanocubes was higher than Ag nanosphere. Most of the research focused on the influence of size and shape of single Ag NPs on SERS, but the correlation among Ag NPs size distribution, coverage, and morphology on GS towards SERS enhancement is rather neglected.

Here we demonstrated a simple and easy-to-implement method to prepare Ag NPs/GS hybrid SERS substrate. We try to study the controllable decoration and SERS β_{EF} of the hybrid substrate from three aspects as Ag NPs size distribution, morphology, and coverage on GS.

2. Materials and Experimental Section

2.1. Materials. Cu foil was employed as the graphene sheet (GS) substrate. Polymethyl methacrylate (950 PMMA A6, 6% in anisole, Nippon Kayaku Co., Japan) was used as the medium for transferring the GS. Silver nitrate (98% AgNO_3) was purchased from Shanghai Chemical Reagent Co. All chemicals were of analytical grade and were used as received without further purification. Deionized water (DI water, resistivity $> 18.0 \text{ M}\Omega \text{ cm}^{-1}$) was used during the sample preparation.

2.2. Synthesis of Few-Layer GS Decorated with Ag NPs. GS growth by low pressure chemical vapor deposition (CVD)

on copper (Cu) substrate was firstly cleaned with deionized (DI) water and dried in nitrogen. Subsequently, 1 mM AgNO_3 (silver nitrate) solution was prepared by adding 17 milligram AgNO_3 to 100 milliliter DI water and used as aqueous metal precursor. Then GS were immersed in silver nitrate solution for different time spans for decoration of Ag NPs. The samples were marked as A–F accordingly in Table 1.

2.3. Characterization and SERS β_{EF} Measurements. The size distribution, morphology, and coverage of the Ag NPs decorated on GS are investigated using scanning electron microscopy (S-4800 Field Emission Scanning Electron Microscope, SEM) images which are taken with an acceleration potential of 5 kV. The chemical composition of the prepared Ag NPs on GS hybrid was examined by SEM coupled with energy dispersive X-ray spectroscopy (EDS). The crystal structures of the samples were characterized by X-ray diffractometer (Rigaku XRD-6000) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418$).

Raman spectra were recorded on a confocal microscope Raman spectrometer (Horiba JY HR800, France) employing an He-Ne laser operating at 633 nm with an output power of 17 mW. A 100x objective lens was used to focus the laser on the sample. The acquisition time for each measurement was 10 s. All of the Raman spectra data were FFT filtering.

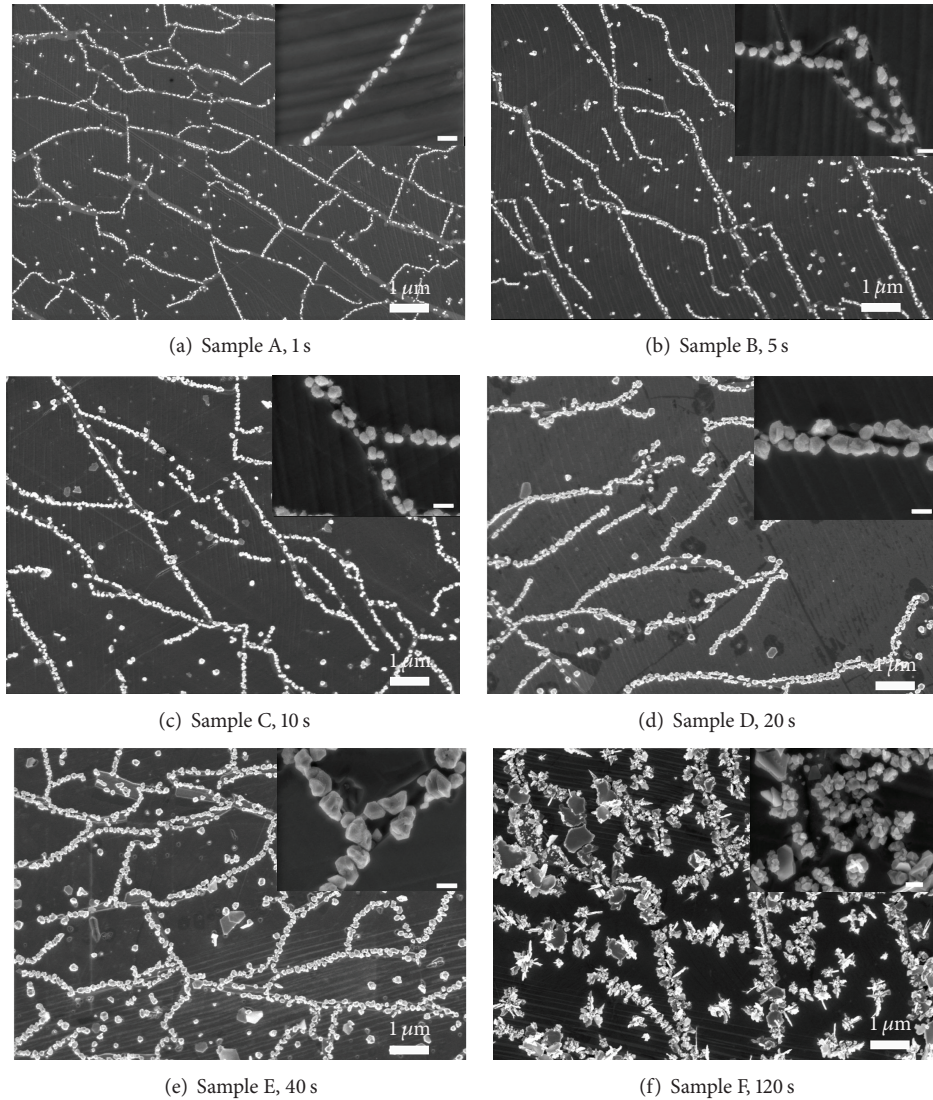


FIGURE 2: SEM images of sample A to F for different immersing time spans (white reticular lines are the grain boundary of single crystal graphene domains). The coverage of the Ag NPs decoration varied from 7.5% for 1 s (sample A) to 19.1% for 40 s (sample E). The Ag NPs prefer to decorate along the boundaries of graphene domain. The diameter of spherical Ag NPs is varied from 10–40 nm for 1 s to 80–140 nm for 40 s. The quasi cubic Ag NPs aggregate along the boundaries of graphene domains and form a quasi-continuous film when the immersing time is longer than 2 minutes. All scale bar $1\ \mu\text{m}$ and inset $100\ \text{nm}$.

TABLE 1: Size distribution and coverage of Ag NPs decorated on GS at different immersing time.

Sample	Morphology	Immersing time/s	Coverage/%	Size/nm
A	Spheric	1	6.5	10–40
B	Spheric	5	7.9	20–50
C	Spheric	10	10.2	30–80
D	Spheric	20	12.6	50–100
E	Spheric	40	19.1	80–140
F	Quasi cubic	120	31.4	20–200

3. Results and Discussion

3.1. Controllable Deposition of Au NPs on GS. Electroless deposition technique is based on the spontaneous oxidation-reduction reaction between substrate surface and metal ion

in solution under the condition that the redox potential of the substrate surface is lower than that of ion in solution. In our case, silver ion with standard redox potential (+0.80 V), which is higher than that of copper (+0.34 V), which is GS growth substrate, can be electroless deposited.

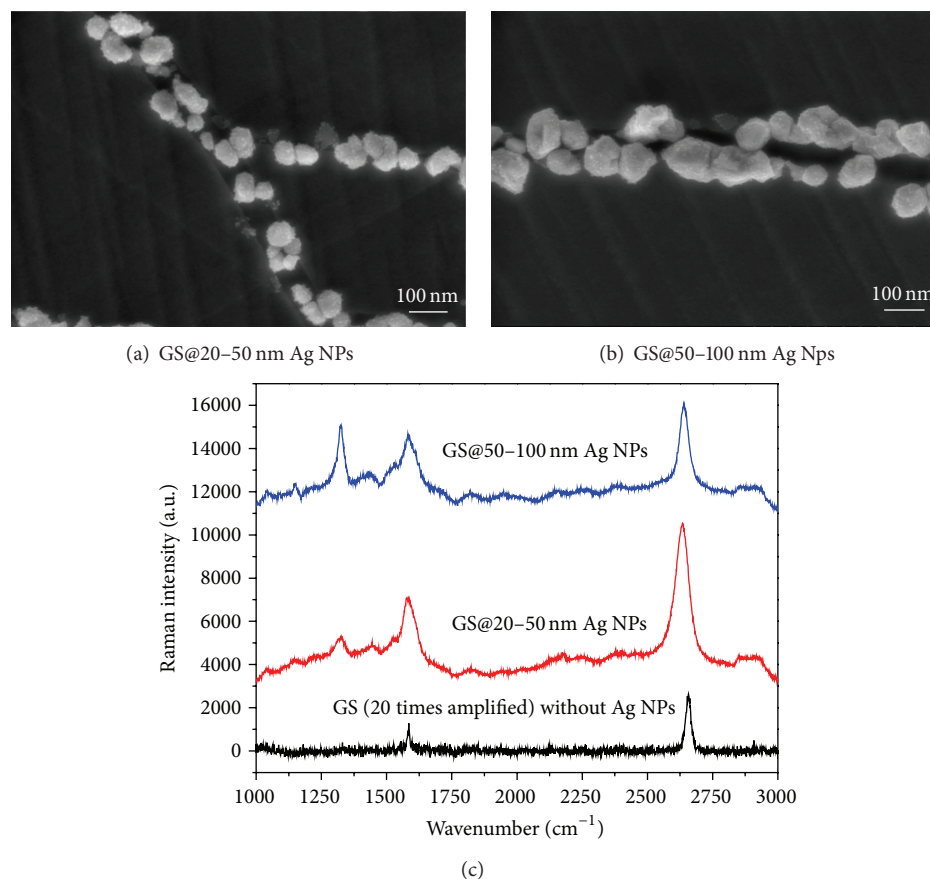


FIGURE 3: SEM images of Ag NPs on GS with different size distribution of (a) 20–50 nm and (b) 50–100 nm. (c) Corresponding SERS spectra of GS with (blue and red) and without (black one which has been amplified 20 times) Ag NPs decoration. Scale bar 100 nm.

In order to verify the decoration of Ag NPs on GS, EDS analysis is employed to examine the chemical composition of samples. Sample A to E are spherical while sample F is quasi cubic in morphology as shown in Table 1. For the spherical sample, A is the shortest immersing time spans, 1 second, and E is the longest, 40 seconds, in AgNO_3 , respectively. The normalized EDS spectrums of samples A and E are shown in Figures 1(a) and 1(b), respectively. The Ag peak is noticeable, together with small C peak and the dominant Cu peak from the copper which is GS growth substrate. Quantitative analysis revealed an Ag composition of 6.10% and 12.68% for samples A and E, respectively. This indicates that the composition of Ag increased with the immersing time spans.

The X-ray diffraction (XRD) patterns of the samples before and after Ag NPs decoration are shown in Figure 1(c). The sample without Ag NPs has only two diffraction peaks at 50.5° and 43.6° in spectrum A (green line), corresponding to the characteristic peak of Cu (200) and (111) since the growth substrate copper foil is polycrystalline in structure with grain orientation of mainly (200) and a few (111). Sharp diffraction peak at 38.1° is observed in both spectrum B (blue line) and spectrum C (red line), corresponding to Ag (111), which further confirmed the formation of single crystalline silver (JCPDS 04-0783) on GS after the GS immersing in AgNO_3 precursor solution.

Figure 2 demonstrated the SEM images of Ag NPs decoration on GS after immersing in 1 mM AgNO_3 for different time (in this paper we have only compared different immersing times under 1 mM AgNO_3 solution concentration). These images clearly revealed that Ag NPs favor decorating on the boundaries of graphene domains; on the contrary only a few of Ag NPs deposited inside. In the whole substrate point of view Ag NPs decoration tends to be uniform as shown in Figure 2. We tried controllable preparation of Ag NPs on GS from three aspects of size distribution, morphology, and coverage control. Firstly, the size distribution of Ag NPs decorated along the boundaries varied in the range of 10 to 140 nm when the increasing immersing time increased from 1 s to 40 s. Secondly, Ag NPs were spherical in morphology under shorter immersing time as samples A–E (Figures 2(a)–2(e)). And when the immersing time span is more than 2 minutes, the Ag NPs were found to transform into quasi cubic as sample F (Figure 2(f)). Finally, the controllable coverage, which is defined as the number of Ag NPs within $10 \mu\text{m}$ length along graphene domain boundary, changing from 7.5% (Figure 2(a)) to 19.1% (Figure 2(e)), was also achieved in our experiments by varying the immersing time span. The morphology, size distribution, and coverage of Ag NPs decorated on GS under different immersing time span were summarized in Table 1.

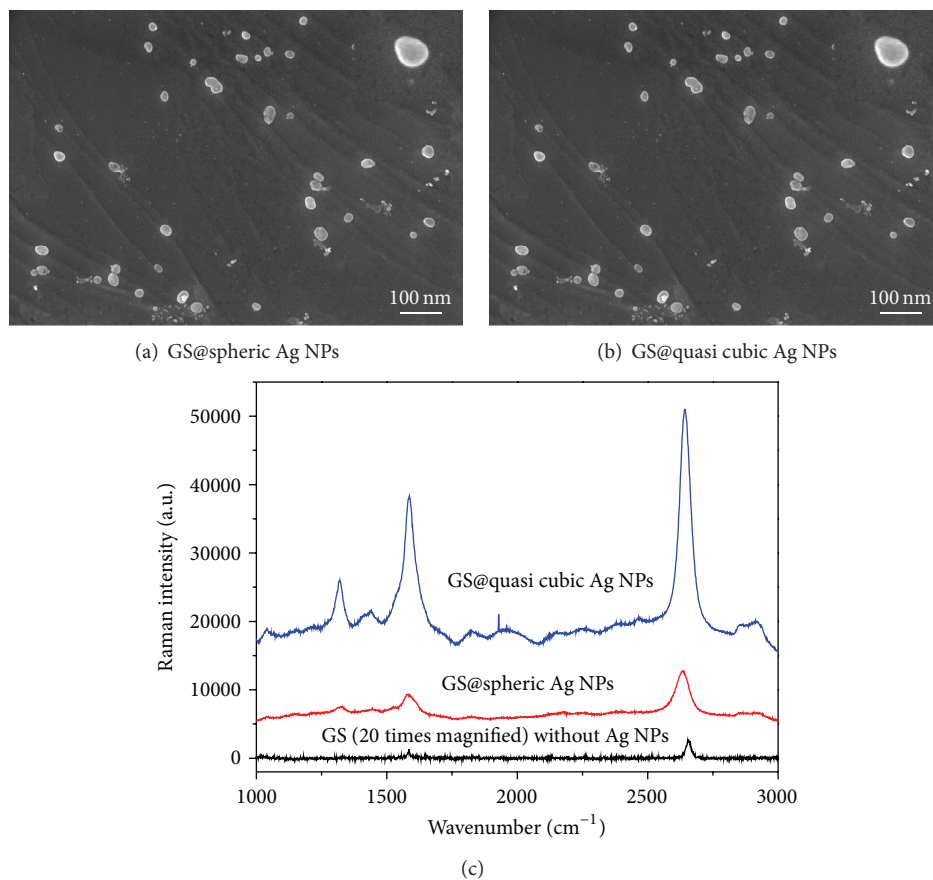


FIGURE 4: SEM images of GS decorated with morphologies of (a) spheric and (b) quasi cubic Ag NPs. (c) Corresponding SERS spectra of GS with Ag NPs decoration (blue one for quasi cubic and red one for spheric one) and without Ag NPs decoration (black one which has been amplified 20 times). Scale bar 100 nm.

3.2. Raman Spectra of GS and Ag NPs on GS Hybrid. According to the size distribution, morphology, and coverage of Ag NPs controllably decorated on GS, SERS β_{EF} of the Ag NPs on GS hybrid substrate are investigated.

Figure 3(c) shows the Raman spectrums of GS before and after being decorated with Ag NPs. The β_{EF} can be calculated by comparing Raman peaks of pure GS with that of Ag NPs on GS hybrid. The β_{EF} of G peaks and 2D peaks are estimated to be 47, 50 for Ag NPs in size distribution of 20–50 nm (red) and 42, 31 for 50–100 nm (blue), respectively. Obviously, both G peak and 2D peak have been significantly enhanced after Ag NPs decoration, and Ag NPs size distribution has an effect on β_{EF} . The 2D peaks β_{EF} of 20–50 nm Ag NP is 1.6 times in average better than that of 50–100 nm, which means average value of β_{EF} 1.6 times SERS enhanced is detected while the size distribution is reduced to half, which is the same as the result of Kumar et al. who prepared the samples with graphene oxide (GO)/silver composites [10]. It is possible to improve the enhancement factor of SERS by controlling of Ag NPs size distribution: the smaller the size of distribution is, the stronger the enhancement factor of SERS is.

As can be seen from Figure 4, despite having almost the same size distribution, quasi cubic Ag NPs (Figure 4(b)) give rise to stronger SERS peaks compared to that of spheric one

(Figure 4(a)). The quasi cubic Ag NPs SERS enhancement factors β_{EF} (blue in Figure 4(c)) of D peaks and 2D peaks are measured to be about 6.53 and 4.94 times in average value stronger than that of spheric Ag NPs (red in Figure 4(c)) and 307 and 247 times in average value stronger than that of pure GS without Ag NPs (black in Figure 4(c)), respectively. This is attributed to the more intense local electromagnetic fields generated around the sharp edges and vertices of the quasi cubic structure [20] and consistent with the result of about 8 times than that of spheric Ag NPs on GO [9]. Controllable decoration preparation is crucial for improving SERS enhancement factors β_{EF} , since the quasi cubic Ag NPs on GS SERS enhancement factors β_{EF} are 6.53 times in average value stronger than that of spheric one.

Figure 5 indicated that the coverage of Ag NPs decorated on GS has an influence on the SERS signals of the Ag NPs/GS SERS substrate. The higher Ag NPs decoration coverage of 12.6% SERS enhancement factors β_{EF} (blue in Figure 5(c)) of G peaks and 2D peaks is measured to be about 2.3 and 1.62 times in average value stronger than that of lower coverage 6.5% (red in Figure 5(c)) and 47 and 50 times stronger than that of GS without Ag NPs (black in Figure 5(c)), respectively. When the coverage increases one time, β_{EF} is nearly doubled in average value. Due to the increasing coverage, the “hot

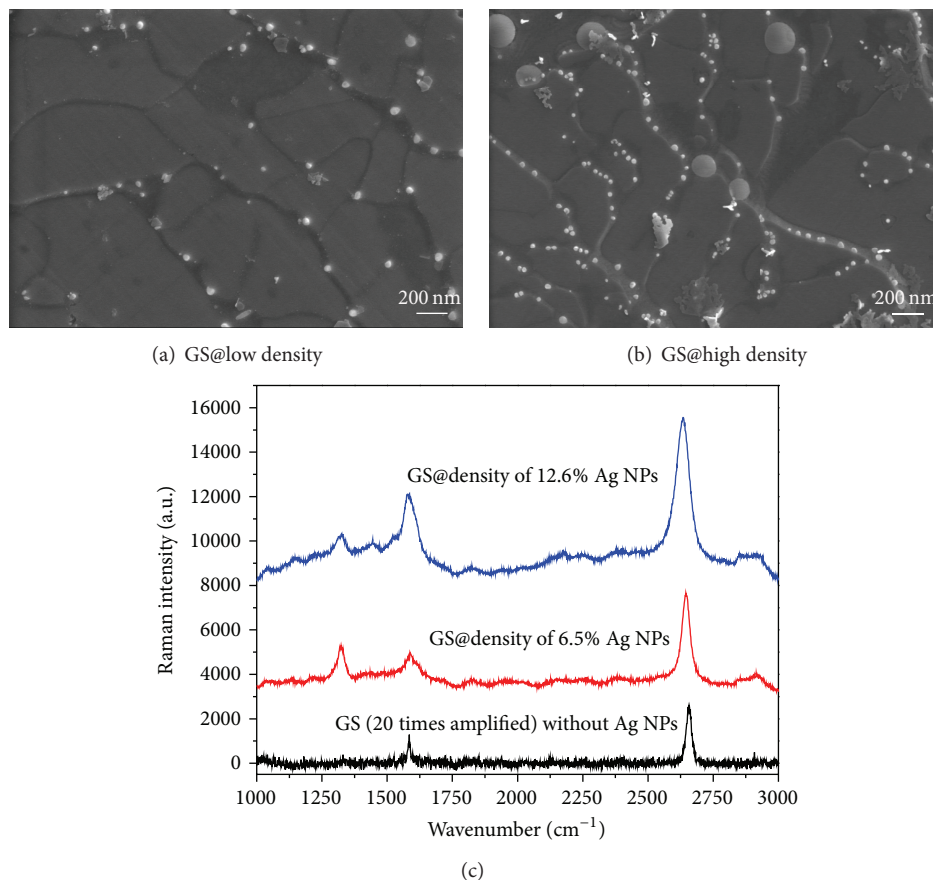


FIGURE 5: SEM images of GS decorated with Ag NPs coverage of (a) 6.5% and (b) 12.6% in almost the same size distribution. (c) Corresponding SERS spectra of GS with Ag NPs decoration (blue one for 12.6% and red one for 6.5% coverage) and without Ag NPs decoration (black one which has been amplified 20 times). Scale bar 200 nm.

spot” which contributes to SERS enhancement became much more resulting in higher β_{EF} for SERS substrate.

4. Conclusion

Studying the SERS performance of plasmonic metal nanoparticles (NPs)/GS hybrid materials is important for direct probing of the chemical effect of GS on plasmonic NPs. By taking advantage of both traditional metallic substrate and graphene substrates, we successfully decorated Ag NPs on CVD growth GS where size distribution, morphology, and coverage of Ag NPs could be conveniently controlled by carefully manipulating the electroless deposition conditions. Maximum 200–300 times average value enhanced SERS intensities are detected from the Ag NPs on GS hybrid substrate as compared to pure GS substrate. The quasi cubic Ag NPs on GS SERS enhancement factors β_{EF} are 6.53 times in average value stronger than that of spheric one; 1.6 times average value SERS β_{EF} is detected while the size distribution is reduced to half, and when the coverage increase is doubled, β_{EF} is nearly doubled. Controllable decoration preparation is crucial for improving SERS enhancement factors β_{EF} . The simple methods of preparing SERS substrate will facilitate the

wide application of SERS effect and efficiently improve SERS performance towards sensing applications.

Conflict of Interests

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

Acknowledgments

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