Rationally Designed Graphene/Bilayer Silver/Cu Hybrid Structure with Improved Sensitivity and Stability for Highly Efficient SERS Sensing

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Supporting Information

ABSTRACT: A simple and cost-effective strategy was rationally designed to fabricate a special sandwich structure consisting of graphene, bilayer silver, and a copper plate, which was used as a surface-enhanced Raman scattering (SERS) substrate for highly efficient SERS sensing and detection of trace molecules. Silver dendrite (AgD) nanostructures were subsequently grown on a silver nanosphere (AgNS)/Cu surface to form a bilayer silver/Cu structure, which showed a 1.5-fold Raman enhancement compared to that of the AgNS/Cu substrate. After depositing graphene on the bilayer silver/Cu substrate to obtain a sandwich structure, a higher SERS enhancement and better durability were enabled. The SERS performances, measured by a portable Raman instrument, showed that the optimized sandwich structure substrate exhibited high SERS sensitivity to crystal violet (CV) and rhodamine 6G (R6G) with low limit of detection of $10^{-9}$ and $10^{-8}$ M, respectively. Such a sandwich-structured substrate exhibited good reproducibility across the entire detection areas with an average relative standard deviation less than 5.9%, which permits its reliable quantitative detection of CV and R6G molecules. In addition, graphene both effectively improved the SERS performances and protected Ag nanocrystals from oxidation, which endowed the sandwich structure a long-term stability with deviation of characteristic peaks intensity lower than 3.6% after 25 days. This study indicates that the graphene/bilayer silver/Cu sandwich structure as a SERS substrate has a great potential in detecting environmental pollutants.

1. INTRODUCTION

Trace- and ultratrace-level analyses of (bio)chemical molecules are relevant to several fields including chemistry, environmental science, medicine, and bio-related systems. Liquid chromatography/mass spectroscopy, high-performance liquid chromatography, and immunoassays are general approaches used for molecular detection. Although very effective and accurate, they are time-consuming and costly. Surface-enhanced Raman spectroscopy (SERS) is an emerging and powerful tool for nondestructive identification and sensing of molecular species owing to its extraordinary sensitivity and selectivity reaching single to few molecules detection. More importantly, the Raman signal is free from water interference and thus makes it suitable for the detection of aqueous samples. It is reported that surface-enhanced Raman scattering can enhance normal Raman signal up to $10^6$--$10^{12}$ times on the basis of the enhanced local electromagnetic (EM) field near the noble-metal-nanostructured surfaces. Hence, molecular detection and sensing based on surface-enhanced Raman scattering can be achieved using SERS active noble-metal micro/nanostructures as plasmonic antennas to magnify the Raman signals.

When analyte molecules are adsorbed on a roughened metal surface (i.e., Pt, Ag, and Au nanoparticles (NPs)), it leads to strong Raman enhancement of the analytes’ signals, which is caused by the electromagnetic (EM) and the chemical effect. According to electromagnetic mechanism of SERS, the electromagnetic “hot spot” occurs near the sharp tips and protrusions and also forms at the smaller gaps in nanometer scale between metal nanoparticles (NPs) and nanofilms. For example, Mihi and co-workers fabricated a rough silver film showing the enhancement factors (EF) for benzenethiol of $10^7$ and 4-mercaptopyridine of $10^{10}$. Amanda J. Haes demon-
stated that rough Au nanostars showed an enhanced signal from electromagnetic coupling between Au nanostars, and a low concentration of 100 nM for uranyl was detected.14 MacFarlane et al. reported a porous gold metamaterial that exhibited a joint EM field enhancement resulting in a limit of detection (LOD) of $1 \times 10^{-13}$ M and the coefficient of variation of 21%.15 Recent progress allows molecular detection using the portable Raman spectrophotometers for rapid and on-site detection.16,17 However, the SERS substrates possessing both high detection sensibility and high reproducibility remains a problem. Encouragingly, novel sandwich configurations have been demonstrated to help the production of even higher enhancement by an order of $10^3$ due to the coupling of localized surface plasmon resonance (LSPR) from the metal nanostructures with uniform Raman signals. To date, many efforts have been made to develop sandwiched SERS substrates to exploit the coupling of LSPR either between two metal nanostructured thin film layers or one nanoparticle and one metal film layer.18,19 Kuang et al. have fabricated a sandwich structure of roughened Ag slice/target protein complexes/fi metal layer.20 More recently, Wang et al. reported a flexible sandwich structure consisting of PMMA, Ag nanoflowers, and monolayer graphene for ultrasensitive, reproducible, and stable SERS detections and showed that the LOD for rhodamine 6G is down to $10^{-14}$ M with relative standard deviation lower than 10%.21

Despite the superior enhancement ability of Ag-based nanostructures, the oxidation commonly occurs on the surface and is still unavoidable; such SERS substrates have difficulties in maintaining their long-term stability and reproducibility. In this regard, the graphene-decorated noble-metal-nanostructured hybrid SERS substrates have drawn significant attention because of the synergistic effect of noble-metal’s high SERS activity and graphene’s intriguing Raman scattering properties originating from its atomic thickness and unique electron, phonon structures. Recent studies have proved the important roles of graphene in these hybrid structures, including as an oxidation preventer,22 fluorescence quencher,23 additional chemical enhancer,24 and molecule stabilizer and absorber.25 More importantly, graphene is cheap and has an abundant material source, greatly improving its feasibility for practical applications. Recently, various methods have been developed for the synthesis of graphene. Among them, chemical vapor deposition26,27 has proven to be the most commonly used method for high-quality graphene fabrication. Chemical reduction of graphite oxide (GO), however, is one of the conventional methods for large-scale synthesis of graphene.28

In the process, GO is readily and efficiently prepared by the Hummers method in the lab, followed by the reduction with a reducer.29

By combining the superior plasmonic properties of silver with the advantages of graphene, we demonstrated a sandwich-structured SERS substrate consisting of graphene/AgD/AgNS/Cu fabricated by a facile, cost-effective, and practicable synthetic strategy. The fabrication process mainly consists of three steps, as shown in Figure 1. The sandwich structure exhibited an improved Raman intensity of 2.3-fold compared to that of the AgNS/Cu substrate, and the LODs for CV and R6G molecules are $10^{-9}$ and $10^{-8}$ M, respectively. In addition, remarkable SERS reproducibility with the standard variation of 5.865% was exhibited by the sandwich structure. An improved SERS signal long-term stability was achieved by coating a graphene layer.

2. RESULTS AND DISCUSSION

2.1. Morphologies and Microstructures of the Products. The actual typical scanning electron microscopy (SEM) images of the products fabricated at different steps are shown in Figure 2. Figure 2a displays that uniform Ag nanospheres with a rough surface structure and a diameter of about 200 nm are prepared on the Cu plate. Figure 2b presents the image of AgD/AgNS on a Cu plate, in which a layer of hierarchical dendritic Ag nanocrystals with trunk diameter ranging from 70 to 90 nm is synthesized on the surface of a AgNS/Cu plate. GO-coated samples are shown in Figure 2c, indicating the sandwich structure of GO/bilayer silver/Cu. Figure 2d–h shows a magnified image of graphene/AgD/AgNS/Cu and corresponding Energy dispersive spectroscopy (EDS) elemental mapping images. It is clear that GO and graphene films on the Cu support have flake-like forms of different sizes and their size is usually more than 2 μm. EDS mapping analysis displays the uniform distribution of three typical elements of C, Ag, and Cu. Additionally, Raman spectra of the products shown in Figure 2c,d were recorded to illustrate the transformation from GO to graphene. The Raman spectra (Figure S1) show D peak of 1352 cm$^{-1}$ and G peak of 1591 cm$^{-1}$, confirming the existence of GO in a GO/bilayer silver/Cu sandwich structure.30 From the analysis of the graphene spectra, we suppose that the GO-coated sample has been reduced to graphene in the sandwich structure.31

2.2. Formation Process of the Graphene/Bilayer Silver/Cu Sandwich Structure. The fabrication of the graphene/AgD/AgNS/Cu sandwich structure involves three main steps: preparation of AgNS on a Cu plate, depositing AgD onto the AgNS/Cu substrate to form a bilayer silver/Cu structure, and coating graphene onto the surface of the AgD/AgNS/Cu substrate to construct a sandwich structure. In the present synthesis system, potassium biphthalate played a crucial role in the preparation of the bilayer silver structure on Cu plates. The products were only Ag dendritic nanostructures on a Cu plate in the absence of potassium biphthalate (Figure S2). It is also important to first mix AgNO$_3$ with potassium biphthalate in an aqueous solution for 10 min, which allows the coordination reaction between AgNO$_3$ and potassium biph-
thalate to form a coordination compound precursor. We conducted time-dependent experiments at varying stages to reveal the morphology evolution in the formation of the bilayer Ag on a Cu plate. First, when a Cu plate was put into the above mixture solution, it rapidly reacted with the free Ag ions by a galvanic replacement reaction\(^3\) and tiny Ag nanoparticles were immediately formed on the Cu plate. The Ag nanoparticles gradually grew up until the free Ag ions were exhausted for 4 min (Figures S3 and 3a), and they grew into rough Ag nanospheres with particle size increased to 200 nm (Figure 2a). Then, the coordination compound precursor of Ag ions began to react with the Cu plate, and it produced dendritic Ag nanostructures on the AgNS/Cu substrate to form a bilayer silver/Cu structure (Figure 3b). Further prolonging time resulted in large quantity of Ag dendritic structures, as shown in Figure 3c–f. The evolutionary process could also be characterized by X-ray diffraction (XRD) analysis. XRD patterns (Figure S4) of the samples prepared at different stages showed that the weak Ag diffraction peak of (111) appeared for 3 min, which confirmed that AgNS was initially formed on the Cu substrate surface. It was found that the diffraction peak intensity of Ag increased with the increasing reaction time, accompanied with the decrease in the intensity of Cu plate diffraction peaks. It indicated that more AgD structure was deposited on the AgNS/Cu substrate. It must be noted that potassium biphthalate served as an important structure-director for the construction of bilayer silver/Cu structures.

In addition, the effect of different molar ratios of AgNO\(_3\) to potassium biphthalate on the morphology of bilayer silver/Cu substrates was also investigated (Figure S5). Tuning the molar ratio from 2:1 to 16:1 always resulted in a bilayer silver/Cu structure. However, the sizes and contents of AgD and AgNS varied with the molar ratio. For example, large-sized AgD on the Cu plate surface was obtained at a low molar ratio (2:1) of

Figure 2. SEM image of (a) AgNS on a Cu plate, (b) AgD/AgNS on a Cu plate, (c) graphene/AgD/AgNS on a Cu plate, (d) selected area of graphene/AgD/AgNS on a Cu plate, and (e–h) corresponding EDS elemental mapping images.

Figure 3. SEM images of a Ag/Cu substrate fabricated at different reaction times (a) 3 min, (b) 5 min, (c) 6 min, (d) 8 min, (e) 10 min, and (f) 15 min.
Figure 4. SEM images of a GO-coated bilayer silver/Cu substrate prepared at different coating times (a) 6 min, (b) 8 min, (c) 10 min, (d) 12 min, (e) 14 min, and (f) 16 min.

Figure 5. SERS spectra of AgD/AgNP/Cu substrates prepared at different reaction times (a) and molar ratio of AgNO₃ to potassium biphthalate (b). SERS spectra of graphene/AgD/AgNP/Cu substrates prepared at different GO concentrations (c) and GO electrodeposition times (d). All of the substrates were immersed in CV molecules of $10^{-6}$ M for 12 h and dried for SERS detection.
AgNO₃ to potassium biphthalate (Figure S5a). With the increasing molar ratio, the size of AgD became smaller. Meanwhile, a large quantity of AgNS was formed on the surface of the Cu plate. At molar ratio of 18:1, more Cu reacted with free Ag ions, resulting in some microholes on the Cu plate. Thus, an appropriate molar ratio of 4:1 was proposed to obtain bilayer silver/Cu substrates.

To further enhance the SERS sensitivity and the long-term stability of the bilayer silver/Cu substrates, a designed sandwich structure was constructed by depositing a layer of GO on the surface of bilayer silver/Cu via an electrodeposition method. Electrodeposition represents a faster and more effective method for depositing GO on the substrates. Figure 4 shows the SEM images of GO-coated bilayer silver/Cu substrates fabricated at different coating times of GO. When it was deposited for 6 min, a thin GO flake was sparsely deposited on the substrate surface (Figure 4a). For 10 min, the surface of the substrate was well coated by a GO film, forming a relative flat surface (Figure 4c). When the coating time was increased to 12 min or more, it was completely coated by GO and a thick GO film was obtained (Figure 4e,f). In addition, it was found that the GO concentration also influences the coverage and thickness of the GO film on the substrates, as shown in Figure S6. GO concentration of 5 mg L⁻¹ was selected for the coating process. Finally, a GO/bilayer silver/Cu sandwich structure prepared by the optimizing conditions was further reduced by ascorbic acid in-situ to transform GO to graphene. The resultant graphene/ bilayer silver/Cu sandwich structure was obtained and served as a SERS substrate.

2.3. SERS Sensitivity of the Samples. As expected, we found that different structures of monolayer AgNS/Cu, bilayer AgD/AgNS/Cu, and sandwich-structured graphene/bilayer silver/Cu could exhibit varying degrees of SERS sensitivities. Thereby, we first examined their SERS performances using CV as probing molecules. These structures as SERS substrates could be easily identified by CV molecules using a portable Raman spectrometer. SERS spectra of CV adsorbed on monolayer AgNS/Cu substrates are shown in Figure 5a. All of the Raman peaks could be ascribed to the different vibrating modes of CV, as we reported in the previous work.33,34 We estimated the enhancement factor (EF) of AgNS/Cu, AgD/AgNS/Cu, and graphene/bilayer silver/Cu sandwich structure substrates, and Raman spectra of bulk CV solution of 0.1 M.

We estimated the enhancement factor (EF) of AgNS/Cu, AgD/AgNS/Cu, and graphene/bilayer silver/Cu sandwich structure substrates as follows:

$$\text{EF} = \left( \frac{I_{\text{SERS}}}{I_{\text{bulk}}} \right) \times \left( \frac{N_{\text{bulk}}}{N_{\text{SERS}}} \right)$$

where $I_{\text{SERS}}$ and $I_{\text{bulk}}$ are the intensities of C–H in-plane bending vibrations at 1174 cm⁻¹ in the presence of AgNS/Cu, AgD/AgNS/Cu, and graphene/bilayer silver/Cu sandwich structures and in the absence of metal nanoparticles, respectively (Figure 6). $N_{\text{SERS}}$ and $N_{\text{bulk}}$ represent the numbers of CV molecules in the SERS sample ($10^{-5}$ M) and in the ethanol solution (0.1 M), which were effectively excited by a laser beam. Accordingly, the EF of a AgNS/Cu substrate is 5.37 × 10⁵ and the EFs of AgD/AgNS/Cu and graphene/bilayer silver/Cu sandwich structures are 8.04 × 10⁴ and 1.19 × 10⁵, respectively. The enhancement factor calculation process can be found in the Supporting Information. Owing to the formation of a bilayer silver structure in AgD/AgNS/Cu, the EF of the bilayer silver/Cu substrate shows 1.5-fold improvement compared to that of our AgNS/Cu substrate and the enhancement ability is better than that of the reported AgD/ reduced graphene oxide (rGO) composite with EF of 5 × 10⁴.36 As expected, the graphene/bilayer silver/Cu sandwich structure exhibits much better SERS signal and shows 1.48-fold enhancement than that of a bilayer silver/Cu substrate, which is probably due to more hot spots offered by graphene wrinkles and the improvement of electromagnetic field.25,37 By comparison, the SERS EF of our graphene/bilayer silver/Cu sandwich is greater than that of Cu/AuG, for which the EF value was estimated to be 3.7 × 10⁵.38 The similar synergistic enhancement effect of graphene and metal nanostructures is observed in the graphene/Au NPs, graphene/Au/Si, and graphene/Au or Ag NPs substrates.41,42

2.4. Uniformity and Long-Term Stability of a Graphene/Bilayer Silver/Cu Sandwich Structure Substrate. The uniformity of SERS signal for a sandwich structure substrate was assessed by comparing SERS spectra of CV at 60...
Figure 7. (a) SERS spectra of CV molecules measured on 60 spots of the sandwich structure and (b) comparison of the SERS intensity at 174 cm$^{-1}$ peak for CV.

Figure 8. SERS spectra of (a) CV and (c) R6G with five different concentrations; linear fit between the SERS intensity and target molecules concentration (b) CV and (d) R6G.

different spots on one substrate (Figure 7a). The standard variation for the vibrations of 1174 cm$^{-1}$ is 5.865%, as shown in Figure 7b, exhibiting remarkable SERS reproducibility. Indeed, the signal spatial uniformity of graphene/bilayer silver/Cu may
Figure 9. (a) SERS spectra of freshly prepared and exposed to air for 25 days of the bilayer silver/Cu substrate and graphene/bilayer silver/Cu substrate. (b, c) Comparison of SERS signal intensity at peaks of 725, 1174, and 1587 cm\(^{-1}\) of two sets of substrates.

Figure 10. SERS spectra of CV detected on fish scales with different spraying concentrations using the graphene/bilayer silver/Cu substrate.
detection opens new avenues for rapid and high sensitive analysis of trace molecules in real samples.

3. CONCLUSIONS
A unique sandwich structure based on bilayer silver for the sensitive and quantitative detection of ultratrace analytes using SERS technology was designed and implemented. The sandwich structure consisted of graphene, a bilayer silver nanostructure, and a copper plate. The SERS sensitivity of the sandwich structure could be optimized by tuning the reaction time, molar ratio of AgNO₃ to potassium biphthalate, GO concentrations, and electrodeposition time. The SERS properties of the samples were measured by a portable Raman instrument, and the results showed that the bilayer silver/Cu substrate exhibited a 1.5-fold enhancement compared to the AgNS/Cu substrate. As expected, the graphene/bilayer silver/Cu sandwich structure exhibited the highest SERS signal and shows 2.3-fold enhancement than that of AgNS/Cu substrate. The optimal SERS sandwich structure substrates showed the LOD of 10⁻⁹ and 10⁻⁸ M for CV and R6G, respectively. The most important observation is that graphene/bilayer silver/Cu demonstrated excellent signal uniformity with the standard deviation of 5.865%. Furthermore, it still maintained a good SERS activity after being exposed to air for 25 days. It also showed great potentials in trace detection of real samples. Coupled with the signal uniformity and the long-term stability, our graphene/bilayer silver/Cu substrates are expected to find broad practical applications in outdoor rapid quantitative analysis of chemicals and hazardous pollutants.

4. EXPERIMENTAL SECTION
4.1. Synthesis of AgD/AgNS on a Cu Plate. Copper (Cu) plate is chosen as an attractive SERS substrate because it is cheap and more effectively couples with silver. The Cu plate was first cut into pieces of 1.5 cm × 1.5 cm and cleaned for further use. Then, the Cu plate was immersed into a mixed aqueous solution (20 mL) of AgNO₃ (0.5625 mmol) and potassium biphthalate (0.1406 mmol) for different periods of time (3–15 min). Uniformly distributed Ag nanospheres (AgNS) were initially formed on the Cu plate by a galvanic replacement reaction. Then, Ag dendrites (AgD) were grown on the surface of AgNS to form a bilayer structure. The obtained bilayer silver on the Cu plate was cleaned and dried under N₂ gas flow.

4.2. Synthesis of a Graphene/Bilayer Silver/Cu Sandwich Structure. Graphene oxide (GO) was synthesized by the modified Hummers method. GO-diluted solution with concentration of 5 mg L⁻¹ was obtained by dispersing original GO solution into water and ultrasonication for 60 min. The above samples were decorated with GO to form a sandwich structure via an electrodeposition method. Briefly, a clean platinum plate was used as a negative electrode and a bilayer silver/Cu plate was used as a positive electrode. The two electrodes were fixed and kept at a distance of about 20 mm from each other. When the voltage (30 V) was applied, the negatively charged GO nanoflakes moved to the negative electrode and then deposited on the surface to form a GO/bilayer silver/Cu sandwich structure. Finally, GO was further in-site reduced by ascorbic acid (30 mL, 5.68 mM) to transform GO to graphene, and a graphene/bilayer silver/Cu sandwich structure was obtained and used for SERS substrates.

4.3. Characterization and SERS Measurements of the Products. We used a rotating-anode X-ray diffractometer (Rigaku D/Max-γA) to characterize the phase and composition of the products. The morphologies were observed by a scanning electron microscopy (SEM, Quanta 200 FEG). Energy dispersive spectroscopy (EDS) equipped on a field-emission SEM (JEOL-JSM-6700F) was used to measure the elemental mapping images. The SERS spectra were recorded by a portable Raman instrument (i-Raman plus, B&K Tek Inc.). For SERS measurements, the SERS substrates were put into different concentrations of analyte solutions with total volumes of 200 μL for a period of 12 h. Then, the substrates were taken out, washed with ethanol and water, and dried for the subsequent Raman measurements. During SERS experiments, a 20X objective in a microscope was used. A 785 nm laser wavelength was selected for excitation, and the total accumulation time was 2 s.

ASSOCIATED CONTENT

■ Supporting Information
The Supporting Information is available free on the ACS Publications website at DOI: 10.1021/acsomega.8b00565.

Raman results, XRD patterns, SEM images, SERS spectra, and calculation of SERS enhancement factor (PDF)

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Notes
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