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Growth graphene on silver–copper nanoparticles by chemical vapor deposition for high-performance surface-enhanced Raman scattering

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ABSTRACT

We present a graphene/silver–copper nanoparticle hybrid system (G/SCNPs) to be used as a high-performance surface-enhanced Raman scattering (SERS) substrate. The silver–copper nanoparticles wrapped by a monolayer graphene layer are directly synthesized on SiO_2/Si substrate by chemical vapor deposition in a mixture of methane and hydrogen. The G/SCNPs shows excellent SERS enhancement activity and high reproducibility. The minimum detected concentration of R6G is as low as 10^{-10} M and the calibration curve shows a good linear response from 10^{-6} to 10^{-10} M. The date fluctuations from 20 positions of one SERS substrate are less than 8% and from 20 different substrates are less than 10%. The high reproducibility of the enhanced Raman signals could be due to the presence of an ultrathin graphene layer and uniform morphology of silver–copper nanoparticles. The use of G/SCNPs for detection of nucleosides extracted from human urine demonstrates great potential for the practical applications on a variety of detection in medicine and biotechnology field.

1. Introduction

Surface-enhanced Raman scattering (SERS) as one of the most powerful probing tools for biochemical applications has received increasing attention [1–3]. To date, the most widely studied SERS platforms are solution-phase Ag, Au and Cu nanoparticles, as enormous Raman enhancement factors could be obtained in areas of "hot spots" from the dispersed nanoscale systems [4]. However, the locations of colloidal aggregations and hot spots in the dispersed nanoscale systems are randomly distributed. Though numerous attempts have been done to design well-ordered Ag or Au nanostructures with high SERS activity [4,5], it is still a challenge to achieve ideal SERS substrates with good stability and reproducibility [6]. Actually, the issue of metal–molecule contact induced signal variations has become a key problem for practical applications [7,8]. The main unfavorable disturbances include charge transfer between the metal and molecules, photo-induced damage and metal-catalyzed side reactions, etc. [6]. Furthermore, the lower adsorption capacity of metal nanostructures for some molecules often limits their applications [9].

Using a thin and pinhole free layer of SiO_2 or Al_2O_3 as an inert shell to isolate metal nanostructures from their surroundings was demonstrated [7]. The main challenge is to get a pinhole-free coating layer with a very small thickness. The atomic thickness and seamless structure of graphene makes it a natural candidate material for shell-isolated SERS. Charge transfer occurs when the graphene Fermi level is located between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of molecules. In the case of charge transfer, the increased separation between negative and positive charges leads to an increase in molecular polarizability that has been associated with larger Raman scattering cross sections [3]. An atomic flat surface of graphene cause a small-distance charge transfer between

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the graphene surface and adsorbed molecules, making the Raman signal more efficiently. Beside the ultrathin structure, graphene also has large specific surface area of 2630 m^2/g [10], which could act as an excellent adsorbent toward organic molecules, especially the aromatic molecules [11,12].

Recently, many studies have been done to obtain graphene–metallic nanomaterials for SERS. These hybrids show great promise for applications in SERS. Ren et al. reported a sensitive SERS substrate for folic acid detection using graphene oxide/Ag nanoparticle hybrids [13]. He et al. demonstrated that the gold decorated graphene can serve as a SERS-active substrate for multiplexing detection of DNA [14]. Murphy et al. reported an enhanced sensitivity for SERS detection based on reduced graphene oxide (rGO)–Ag nanoparticle hybrid [15]. Xu et al. prepared a graphene-veiled gold substrate with a passivated surface for SERS [16]. Chen et al. developed a facile method to fabricate GO encapsulated Ag particles hybrid material as SERS probe [17]. Fan et al. fabricated shape-controlled GO/silver nanoparticle hybrids by immersion method for ultrasensitive single-particle SERS sensing [18]. Xu et al. fabricated graphene/Cu nanoparticle hybrids as surface-enhanced Raman scattering substrate for label-free detection of adenosine [19]. These works provided facile methods to decorate metal nanoparticles on the surface of graphene (or GO) on which the graphene can be as an effective molecule enricher. More reproducible SERS signals were demonstrated in these studies by employing graphene or GO nanosheets as the passivated surface. Nevertheless, there is still a principal disadvantage in signal stability and reproducibility for these methods. As in all the above mentioned methods, the graphene-metal hybrids were obtained either through graphene transferring approach or GO spin-coating scheme. As both approaches essentially belong to physical composition, the tightly sealed structure is hard to form between metallic nanoparticles and graphene layer. The space between graphene and metal nanoparticles will inevitably cause apparent loss of electromagnetic enhancement activity as the electromagnetic enhancement efficiency decays rapidly with distance between the metal nanoparticles and analytes. Moreover, the suspended and wrinkled graphene structures always formed nearby the gaps of nanoparticles [17], making graphene-metal hybrids non-uniform and easy to damage, further reducing the homogeneity and reproducibility of the SERS substrates. Therefore, it is necessary to directly grow a thin layer of graphene onto a good plasmonic nanoparticles, such as sliver and gold. However, many investigations have demonstrated that these noble metals do not support graphene growth. Copper can catalyze graphene growth, but its plasma properties are not as good as sliver.

In this work, we successively fabricate 30-nm silver films and 10-nm copper film SiO_2/Si substrates and obtain uniform silver–cooper nanoparticles by following high temperature treatment in a mixture of methane and hydrogen. Typical chemical vapor deposition (CVD) also happens in this high temperature process and monolayer graphene is simultaneously grown on these nanoparticles and their narrow gaps. As a chemistry composite mode, this method provides an atomically thin, seamless, and chemically inert net to tightly wrap the metallic nanoparticles. Compared with previously reports, this approach exhibits three advantages. Firstly, the direct growth mode make graphene layer tightly wrap the metal nanoparticles, minimize the loss of electromagnetic enhancement activity. Secondly, the direct grown graphene layer is free from suspended and wrinkled structures, thus making SERS substrate more stable and reproducible. Thirdly, direct grown graphene can cover every place of the G/SCNPs, even the narrow gaps of particles. So the target molecules can be more effectively absorbed on the hot spots and thus more sensitive and stable Raman signals are expected. Using G/SCNPs, we succeeded in collecting sensitive and reproducible SERS signals of R6G and discovering the SERS spectral difference of the nucleosides from normal human and breast cancer patients. This work may show great potential for the practical applications of G/SCNPs SERS-active substrate in biological sensing and other biotechnology.

2. Experiment

2.1. Preparation of G/SCNPs

The schematic of preparation process of G/SCNPs was shown in Fig. 1. Silver and copper wire (purity >99.9%) was used as the source for vacuum thermal evaporation. 30-nm silver films (Fig. 1b) and 10-nm copper film (Fig. 1c) were successively deposited on SiO_2 (300 nm)/Si substrates at 10^{-3} Pa at a rate of about 1 Å/s. By considering that silver has much better plasmatic properties than copper and copper is mainly used as catalyst for graphene growth, the proportion of silver and copper in the hybrid film will be closely related to SERS performance. Here, much thicker silver film was employed to get better SERS activity. The fabricated samples were then placed in a quartz tube in a hot wall CVD system. After the vacuum reached a pressure of 10^{-5} Pa, the tube was gradually heated up to 1000 °C with flowing 50 sccm H_2 and 200 sccm Ar at 2000 Pa. The mixture of H_2 and Ar was used to clean the metal film and restrain the metal evaporation during heating process. When the high-temperature zone reached 1000 °C, a mixture of 50 sccm H_2 and 10 sccm CH_4 was introduced into the tube to replace the mixture of H_2 and Ar at a lower pressure of 280 Pa to start graphene growth. After 5 min CVD reaction, the sliver and copper film were melted and aggregated into nanoparticles and were covered with a layer of graphene (Fig. 1d). Finally, the CH_4 was shut off and the quartz tube was rapidly cooled down to room temperature with flowing 50 sccm H_2 and 200 sccm Ar at 2000 Pa.

2.2. Preparation of urine samples

The single, early-morning urine samples were provided by Department of Internal Medicine of Dezhou People's Hospital from volunteers. The samples were centrifuged at a speed of 10,000 rpm for 10 min and the upper liquid was collected for later use. The nucleosides were extracted from urines by affinity chromatography using a phenylboronic acid gel (Affi-gel 601) in a glass column. After the gel was activated and equilibrated with 20 ml of 0.1 M NH_4OAc, 1 ml centrifuged urine was applied to the column. Then the gel was washed with 10 ml 0.1 M NH_4OAc and 10 ml methanol–water (1:1, v/v). The nucleosides were eluted with 10 ml 0.05 M HCOOH in methanol–water (1:1, v/v). Finally, the nucleoside solution was enriched to 1 ml by evaporation for Raman measurements.

2.3. SERS measurements

SERS experiments were carried out using a Raman system (Horiba HR-800) with laser excitation at 532 nm. The excitation laser spot was about 1 μm and the effective power of the laser source was 0.05 mW. Prior to each Raman experiment, calibration of the instrument was done with the Raman signal from a silicon standard centered at 520 cm^{-1}. Subtraction of the baseline using cubic spline interpolation was performed in order to eliminate unwanted background noise and to facilitate data analysis. 10 μL analyte solutions were dispersed on above G/SCNPs using a micropipettor. After being kept under ambient conditions (temperature 25 °C and humidity 55%), the substrate was washed with deionized water and dried under nitrogen at 50 °C. Then the substrates were taken out and fixed onto the glass slide. SERS measurements were taken from at least eight random locations that are more than 3 mm apart with an accumulation time of 30 s.