Research Paper

Reliable molecular trace-detection based on flexible SERS substrate of graphene/Ag-nanoflowers/PMMA

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ABSTRACT

Flexible substrate consisted of PMMA-supported monolayer graphene with sandwiched Ag-nanoflowers (G/AgNFs/PMMA) for ultrasensitive, reproducible, and stable surface-enhanced Raman scattering (SERS) detection is reported. Graphene templated micro-current-assisted chemical reduction method was employed to support AgNFs growth, and uniform-distribution AgNFs with all directions nanotips can generate tremendous enhancement factor and intensive hotspots. The minimum detectable concentration (i.e., detection limit) for rhodamine 6G (R6G) in-situ detection by covering this as-synthesized G/AgNFs/PMMA flexible substrate can be as low as 10^{-14}M. Moreover, graphene can effectively stabilize the SERS signals and protect AgNFs from oxidation, endowing this flexible substrate a long-term stability with maximum intensity deviation lower than 10%, for the quantitative measurements from spot-to-spot or substrate-to-substrate. In order to trial its practical applications with various real-world surfaces, the in-situ SERS detection of phenylalanine@apple, adenosine aqueous solution and methylene-blue@fish was performed by covering this G/AgNFs/PMMA flexible substrate. Clear Raman peaks can be obtained for all the selected samples with concentration of 10^{-10}M and, importantly, good linear relationship between Raman intensity and molecular concentration indicates the potential application of the G/AgNFs/PMMA flexible substrate in quantitative determination. Thus, this high-efficiency and low-cost flexible SERS substrate may provide a new way for the molecular trace-detection in food security and environmental protection.

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1. Introduction

Raman spectroscopy proposed as the molecular fingerprints detection, is a powerful analytical technique in biosensors, chemistry and environmental monitoring, which has received much attention since its discovery [1–3]. However, the application of Raman spectroscopy is extremely limited because the inherent defect of the negligible intensity. Surface-enhanced Raman scattering (SERS) offers a tremendous enhancement of the intensity of vibrational signals over ~10^{10} times, which has opened a new avenue for conventional Raman spectroscopy [2,4]. Over the past two decades, SERS technology as an ultrasensitive, nondestructive, and label-free analytical tool, offered great opportunities in trace-detection of biological and chemical molecules [5–7]. The normally accepted mechanism explanations of SERS activity are electromagnetic enhancement mechanism (EM) and chemical enhancement mechanism (CM) [8]. The enhancement of EM is roughly proportional to $|E|^4$ (E is the intensity of the electromagnetic field) and that can reach ~10^8 or more [9,10]. The enhancement of CM, by contrast, is feeble with 10–100 [10,11]. Some works have revealed that CM is derived from the charge transfer between the molecule and substrate [11], briefly, the polarizability of the molecule increases along with the positive and negative charge become more separated and, therefore, the cross section of the Raman scattering increases [12]. Commonly, the EM-based SERS substrates primarily are noble-metals, such as Ag, Au, Cu and Pt in the form of rough surfaces or nanostructures. However, such kind of SERS substrates is always a

"double-edged sword": (i) the tremendous enhanced electromagnetic field gives Raman signals a significant enhancement, so-called the EM [5,10]; (ii) the inescapable metal-molecule interactions can cause the molecular deformation and signal distortion [13]. Beyond that, the oxidation of metal nanostructures also is "a hot potato" and, thereby, this kind of SERS substrates is difficult to maintain the durable stability and reproducibility. Recent years, a new perspective of strategies towards metal molecule isolation (for more intrinsic and reproducible SERS signals) have been demonstrated [14], which is a revolutionary step in the development of SERS but not the terminal point. A fashionable trend, flexible substrates have been proven to be a fascinating selection for the exploration of SERS in real-world applications [15].

Graphene, a two-dimensional honeycomb lattice of sp^2 bonded carbon atoms, has attracted worldwide interest due to its unique physical properties and potential applications in many fields [16–18]. The extremely high carrier mobility, high transparency and biocompatibility make graphene a promising material in a wide range of applications, including electronics, optoelectronics, batteries, sensors, and supercapacitors [19–21]. Recent years, it was discovered that the intensities of Raman signal on graphene surface are stronger than that on SiO_2/Si substrate [12]. The following researchers have found that the intensities of Raman signal decrease with an increase in the number of graphene layers [22], and the SERS mechanism of graphene is based on CM [12,23,24]. In the research field of SERS, from then on, two-dimensional materials, as graphene and MoS_2, have become a hot research object. The graphene-based SERS substrates have many excellent properties include that: (i) the excellent biocompatibility makes graphene a molecule enricher [25,26]; (ii) the great chemical inertness and the high optical transmission in the visible range make graphene a natural protection layer of metal nanostructures [27,28]; (iii) the fluorescence quenching effect makes graphene a fluorescence quencher [29]; (iiii) the CM-based SERS effect makes graphene an additional enhancer [30]. These characteristics make graphene a great potential and worth expecting material for SERS. However, the enhancement factor of graphene is weak, so combine graphene with noble-metal nanostructure is the development tendency in the SERS substrates fabrication. The hybrid SERS substrate of graphene and noble-metal nanostructure has the huge enhancement factor due to the combination of both EM and CM. Graphene also can isolate noble-metal nanostructure from the probe molecules, which can prevent the metal-molecule instructions and increase the signal-to-noise ratio. The wonderful biocompatibility of graphene can generate controllable molecular distribution, which can further provide clean Raman signals. In addition, the "protective layer" of graphene can protect the metal nanostructure from oxidation and endow the hybrid SERS substrate a long life [27].

Currently, the most commonly used substrates for supporting SERS activity are silicon wafers and glass slides. However, these substrates have the common disadvantages of brittle, nonflexible and inconvenient. It is obvious that the flexible SERS substrates have some advantages over the conventional rigid substrates in their flexibility to fit with the underlying objects. The flexible SERS substrates fabrication must meet following several requirements: low-cost, high sensitivity and reproducibility, easy of synthesis, and quantity production. Recently, many groups have reported the researches of large-area flexible SERS substrates. Fabrication of large-area flexible SERS substrates using a shadow mask assisted evaporation technique have reported [31]. This method has the advantages of being different and simple types of nanostructures, but whole process of this method is complicated. In further interesting research, cellulose paper has been widely used as a flexible supporting material in various SERS substrates [32–35]. However, the poor optical transparent of the cellulose paper is an inherent

problem that difficult to solve. Singh's group have reported the flexible SERS substrate using an oblique angle deposition (OAD) technique [36]. However, the OAD technique has been so far limited to deposit one-dimensional nanostructures only [15]. Beside the inherent disadvantages of these methods, the detection limit of the most of the reported flexible SERS substrates so far are higher than 10^{-10}M. Over the past few years, there has been overpowering interest in the assembly of graphene with metal nanostructure for SERS-based sensing applications. However, only a few purposes were made towards fabricating flexible SERS substrates using graphene-metal nanostructures. In fact, graphene or graphene oxide can be easily incorporated into many kinds of free-standing flexible substrates [37,38].

Compared with the sphere-shape nanoparticles, noble-metal nanostructures with nanoscale nanotips have much stronger capability in concentrating the plasmon induced electromagnetic field [39–43]. Herein, we report a facile and practicable fabrication method for fabricating the flexible SERS substrate via graphene templated electrodeposition, forming the sandwich structure of graphene/Ag-nanoflowers/polymethyl-methacrylate (G/AgNFs/PMMA). Large-area and uniform-distribution AgNFs located in the middle of the sandwich structure, which can contribute tremendous enhancement factor and intensive hotspots. The minimum detectable concentration can reach 10^{-14}M for rhodamine 6G (R6G) in-situ detection by covering this as-synthesized G/AgNFs/PMMA flexible substrate. It is worth mentioning that the minimum detectable concentration for R6G detection on the precursor substrate (i.e., the AgNFs/G/Cu-55 substrate) can be as low as 10^{-17}M (almost the limit of the SERS technology so far). The more meaningful thing is that we can obtain clear Raman signals for the trace-detection by covering the G/AgNFs/PMMA flexible SERS substrate on the real-world surfaces of phenylalanine@apple, adenosine aqueous solution and methylene-blue@fish, indicating that this as-synthesized flexible SERS substrate is suitable for any arbitrary morphology or aqueous solution surface. Therefore, the G/AgNFs/PMMA flexible substrate can provide a practical SERS active platform for the trace analysis with cost-effective, high reproducibility, sensitivity and stability.

2. Experimental

2.1. Preparation of monolayer graphene

Large-area and monolayer graphene was grown on a Cu foil by using the conventional CVD method and, briefly, the whole growth process can be divided into four steps. First, after cleaned in ultrasonic cleaner, a Cu foil in high purity (99.999%, size of $10 \times 10\,cm^2$) was put in a quartz tube in the tube furnace. Then, the intensity of pressure in the quartz tube was pumped to 10^{-3}Pa using the double-pump system (mechanical pump and molecular pump) and, subsequently, the Cu foil was annealed for 10 min with flowing H_2 of 15 standard-state cubic centimeter per minute (sccm) to remove the residual impurities on the surface. Third, the gas mixture of CH_4 and H_2 was flowed-in the quartz tube with rate of 60 and 15 sccm, respectively, for 20 min at the temperature of 1050 °C to support graphene growth. Finally, the whole device was cooled down to the room temperature by opening the furnace lid with steadily flowing H_2 at rate of 15 sccm.

2.2. Preparation of AgNFs/G/Cu substrates

The large-area AgNFs on the surface of graphene were synthetized using micro-current-assisted chemical reduction method (step 1 in Fig. 1). The whole reaction was carried out in aqueous solution (100 mL) which dissolved with $AgNO_3$ (1.70 g L^{-1}) and cit-