Optics Communications 412 (2018) 28–36

Contents lists available at ScienceDirect

Optics Communications

journal homepage: www.elsevier.com/locate/optcom

A flexible and stable surface-enhanced Raman scattering (SERS) substrate based on Au nanoparticles/Graphene oxide/Cicada wing array

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ARTICLE INFO

Keywords:
SERS
Graphene oxide
Cicada wing
Quantitative detection

ABSTRACT

In this work, we presented an eco-friendly and low-cost method to fabricate a kind of flexible and stable Au nanoparticles/graphene oxide/cicada wing (AuNPs/GO/CW) substrate. By controlling the ratio of reactants, the optimum SERS substrate with average AuNPs size of 65 nm was obtained. The Raman enhancement factor for rhodamine 6G (R6G) was 1.08×10^6 and the limit of detection (LOD) was as low as 10^{-8} M. After calibrating the Raman peak intensities of R6G, it could be quantitatively detected. In order to better understand the experimental results, the 3D finite-different time-domain simulation was used to simulate the AuNPs/GO/CW-1 (the diameter of the AuNPs was 65 nm) to further investigate the SERS enhancement effect. More importantly, the AuNPs/GO/CW-1 substrates not only can provide strong enhancement factors but also can be stable and reproducible. This SERS substrates owned a good stability for the SERS intensity which was reduced only by 25% after the aging time of 60 days and the relative standard deviation was lower than 20%, revealing excellent uniformity and reproducibility. Our positive findings can pave a new way to optimize the application of SERS substrate as well as provide more SERS platforms for quantitative detection of organic contaminants vestige, which makes it very promising in the trace detection of biological molecules.

1. Introduction

SERS has attracted much attention due to its remarkable enhancement, nondestructive detection and high sensitivity for the analysis of various molecules at low concentration. These advantages of SERS technology demonstrated that it has great potential in various fields, including physical chemistry, environmental protection, analytical chemistry, biomedical science and food analysis, etc. [1–6]. Since the technology was available, a considerable number of researches have verified that the SERS technique has enormous advantages over other detection techniques, but the primary SERS mechanism is still under debate. To date, there are two SERS mechanisms which are widely confirmed. Electromagnetic enhancement (EM) which is based on the localized surface plasmon resonance (LSPR) arises from neighboring noble metallic nanostructures. Au, Ag and Cu nanostructures which reveal high performances in EM are the most popular SERS platforms according to the previous studies [7]. Chemical enhancement (CM) arises from the dynamic electron transfer effect between probe molecules and nanostructures [8]. It should be emphasized that the SERS enhanced performance is strongly dependent on the size, the shape, the density, the distribution and the morphology of the noble metal nanoparticles [9]. From the view of SERS enhancement performance, the SERS signal which is exerted by the AuNPs is usually less than that of Ag nanoparticles' (AgNPs). However, the service life of the Ag substrate is short and its application is limited due to the oxidation. Compared with AgNPs, AuNPs benefit of a better environmental stability as well as biocompatibility. More importantly, there is a strong and tunable LSPR in visible and near-infrared spectral regions of AuNPs [10]. As for Cu, it is the easiest one to be obtained among these three noble metallic materials, however, its SERS enhanced effect is the weakest.

In recent years, three-dimensional (3D) noble metallic nanoparticle-decorated substrates with abundant nanogaps ("hot spots") have been fabricated [11], and various 3D nanostructured arrays, such as TiO_2 nanorod arrays, silicon nanowire/nanopillar arrays, carbon nanotube arrays and anodic aluminum oxide (AAO) templates have been reported

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https://doi.org/10.1016/j.optcom.2017.11.075
Received 1 September 2017; Received in revised form 28 October 2017; Accepted 27 November 2017
0030-4018/

to be fabricated as 3D-SERS active substrates which further improve the SERS effect [12–17]. Generally, when they are decorated with AuNPs, these 3D SERS active substrates generate a great number of "hot spots" where the intensity of LSPR increases, thus improving the sensitivity of the SERS substrates [18,19]. Nevertheless, there are many disadvantages in preparing these substrates mentioned above, such as the complicated preparation processes, expensive cost, time-consuming experimentation, stringent laboratory conditions and so on. These shortcomings limit the further development of Raman technology. In order to overcome these problems, some biological materials with almost perfect large-scale and super-hydrophobic microstructures were used to improve the SERS performance. For instance, based on photoreduction effect, two types of butterfly wings decorated with AgNPs were selected as SERS active substrates. The SERS detection limit for the R6G solution was as low as 10^{-9} M, and this hybrid structure was applied to ultrasensitive SERS-based biological assay [20,21]. Modified with AgNPs, CW exhibited the potential as an effective SERS substrate for virus detection [22]. CW proves to have a large number of ordered protrusion nanostructures on the surface with the characteristic of super-hydrophobic structure and less adhesion. Therefore it is suitable to use CW in the substrate for probe molecules to attach and thus increasing the sensitivity of SERS substrate. Meanwhile, graphene oxide (GO) has also drawn considerable attentions in many SERS research fields due to its obvious CM. Because the LSPR is in the terahertz range, there is no EM enhancement [23]. GO is oxygenated with phenolic, carboxyl, and epoxide groups on the planes and edges, making it convenient for further chemical modification and functionality [24]. Besides, GO has a unique property that it could restrain the nanoparticles aggregated and act as a fluorescence quencher for nanoparticles upon laser irradiation. Therefore, if combined with noble metallic nanoparticles, these hybrids will exhibit a synergic effect both EM and CM. Dr. T.A. Nguyen researched a facile process for synthesizing SERS substrate by electrodepositing hierarchical Au nanostructures on an indium tin oxide (ITO) glass modified with GO, the detection limit of crystal violet for this kind of substrate was 10^{-11} M [25]. Furthermore, the SERS-based AuNPs/GO has been applied in the determination of Pb^{2+} in water samples with satisfactory results [26].

Herein, the 3D super-hydrophobic nanostructures of the CW and high sensitivity of GO inspired us to put forward a facile and low-cost method to synthesize a flexible and stable sandwich structure AuNPs/GO/CW substrate. The structure sandwiching GO between CW and AuNPs is designed and the schematic is shown in Fig. 1. In the synthesis process, GO was first deposited on the CW surface by spin-coating method. In this case, the protrusion nanostructures on the surface of CW which acted as rough supports not only effectively increased the specific surface area of GO, but also produced more wavelike corrugations of GO surface. Then the hybrid substrate was modified with AuNPs by physical deposition. Compared with those 2D structures where noble metal nanoparticles were directly decorated on GO, the synthesized AuNPs/GO/CW substrate was more sensitive, environmentally friendly, stable, uniform and reproducible. Meanwhile, the AuNPs/GO/CW substrates gained strong EM enhancement from coupling of LSPR by AuNPs and additional CM enhancement form charge transfer between GO and nearby target molecules. Based on the analysis above, we have demonstrated that the AuNPs/GO/CW substrate showed excellent SERS activity as SERS substrates to detect the probe molecule of R6G with a low concentration.

2. Experimental

2.1. Materials

$AuCl_3 \cdot HCl \cdot 4H_2O$ (99.8%) and $Na_3C_6H_5O_7 \cdot 2H_2O$ (99.9%) were purchased from Aladdin, Shanghai, China. Flake graphite, H_2SO_4, H_2O_2, HNO_3, HCl, acetone, ethanol and R6G were of analytical grade and obtained from Beijing Chemical Works. CW were supplied by Hebei University of Environmental Engineering. Other reagents used in the experiments, unless mentioned otherwise, were of analytical grade and used without further purification. Deionized water (18.25 MΩ) was used for all solution preparations.

2.2. Preparation of graphene oxide

GO sheets were prepared according to the well-known modified Hummers method. First, 69 ml of H_2SO_4 was added to a round-bottom flask, standing for 15 min under the condition of ice bath. Then 2 g of flake graphite was added to the flask slowly and stirred in the ice bath. After reacting for 30 min, 8 g of $KMnO_4$ was added. Subsequently, the color of the mixed solution turned green. The mixed solution was stirred by the magnetic stirrer for 12 h at the temperature of 35 °C;. Then, 46 ml deionized water was added to the flask for 6 times, followed by the addition of 25 ml of H_2O_2 solution (30%). Afterwards, the solid product was separated by centrifuge (4000 r/min, 5 min), and then washed repeatedly with HCl solution (5%) and deionized water for 3 times until the pH became 7 and it was free of impurities. Then, the solid product was smeared to the glass pane placed in a vacuum drying oven and dried at 50 °C; for 12 h. Finally, the solid product was dispersed in 20 ml of deionized water by ultrasonic dispersion.

2.3. Preparation of SERS substrates

Prior to the fabrication of the substrates, the 1×1 cm^2 segments of CW were ultrasonically cleansed with acetone, ethanol and ultrapure water in turn for 5 min each to remove the residual impurities and then naturally dried. The AuNPs/GO/CW substrates were synthesized by the following method. First, GO solution (100 mg/L) was deposited onto the surface of CW by spin-coating method and dried in a vacuum drying oven. The AuNPs was prepared by the modified sodium citrate reduction method. $AuCl_3 \cdot HCl \cdot 4H_2O$ aqueous solution (1%) and $Na_3C_6H_5O_7 \cdot 2H_2O$ aqueous solution (1%) were prepared as reactant solutions. Firstly, 1.0 ml of $AuCl_3 \cdot HCl \cdot 4H_2O$ was added to a three-necked flask which contained 100 ml of deionized water, heated and stirred magnetically until the temperature reached 100 °C. Then, quantitative $Na_3C_6H_5O_7 \cdot 2H_2O$ aqueous solution was quickly added to the $AuCl_3 \cdot HCl \cdot 4H_2O$ solution, and the mixture was slowly stirred by magnetic stirrer for 25 min. Meanwhile, it could be evidently observed that the color of mixed solution changed gradually from mazarine blue to claret-red, indicating the formation of AuNPs. Afterwards, the AuNPs solution was concentrated with centrifuge for 10 min at room temperature. Finally, the prepared AuNPs was decorated on the surface of GO/CW by physical deposition and dried in a vacuum drying oven for 10 min at the temperature of 50 °C, and thus the AuNPs/GO/CW substrates were synthesized for further SERS detection.

It has been demonstrated that the size, density, distribution and morphology of metal nanoparticles had a crucial influence on the performance of SERS substrate [27]. In order to obtain a better SERS performance and determine the influence of the AuNPs size on the SERS performance, different amounts of $Na_3C_6H_5O_7 \cdot 2H_2O$ were added into the same volume of $AuCl_3 \cdot HCl \cdot 4H_2O$ aqueous solution and a series of AuNPs/GO/CW substrates with different size of AuNPs were synthesized. The ratio of $AuCl_3 \cdot HCl \cdot 4H_2O$ and $Na_3C_6H_5O_7 \cdot 2H_2O$ and centrifugal rates the were shown below in Table 1.

2.4. SERS measurements

The Raman measurements were performed at room temperature on the Raman system of LabRAM ARAMIS with 633 nm line laser as excitation source. In this report, R6G was selected as probe molecules with the purpose of determining the SERS performance. R6G solution was prepared with the concentration varying between 10^{-3} M and 10^{-8} M by means of dilution method successively by the factors of 10. Prior to the measurements, a droplet of 10 μL R6G was deposited on