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SERS-active composite based on rGO and Au/Ag core-shell nanorods for analytical applications

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ABSTRACT

This work demonstrated a new method to synthesize the functional hybrid material composed of reduced graphene oxide and Au/Ag core-shell nanorods (rGO-Au@AgNRs). The hybrid material can detect rhodamine-6G (R6G) with an enhancement factor (EF) up to $(5.0 \pm 0.2) \times 10^8$, 4 fold higher than that of the rGO-AuNRs. Comparing with SERS-active substrate Au@Ag (without rGO), the Raman intensity of R6G on the rGO-Au@AgNRs has significant enhancement, especially at the Raman peak of 611 cm^{-1}, around 17 times. We also use rGO-Au@AgNRs to monitor the pesticide thiram at a low level $\sim 10^{-7}$ M and RSD 7.5% at the 561 cm^{-1}. The limit of detection (LOD) of thiram using rGO-Au@AgNRs was low to 5.12×10^{-3} μM, which suggested that the rGO-Au@AgNRs has potential applications in the detection of environment pollutants *etc.*

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1. Introduction

Surface-enhanced Raman scattering (SERS) spectroscopy has been successfully used as a spectroscopic tool for the identification and detection of biological and chemical species [1,2]. Noble metallic elements such as Au, Ag, and Cu exhibit strong SERS activity and always catch significant attention. Because of the anisotropy and prominently Raman reinforcing effect, AuNRs were widely used as SERS substrate and remote-controlled photothermal heating material [3]. SERS is mainly caused by their enhancement of electromagnetic field that was induced by localized surface plasmon resonance (LSPR) [4,5]. AuNRs were commonly characterized by two principal plasmon absorption bands, corresponding to the transverse plasmon resonance (TPR) and the longitudinal plasmon resonance (LPR) modes induced by the oscillation of conduction electrons, the peak of LPR could adjust from Vis to near-infrared [6]. However, comparing with the Au@AgNRs, the Raman enhancement of AuNRs was not sufficient, which limited its applications [7,8].

Au@AgNRs have been regarded as superior alternative to AuNRs for biosensing, mainly because of their combination of the stability of AuNRs and high Raman signal enhancement of AgNRs [9,10]. But the SERS-active composite based on colloidal Au@AgNRs nanostructures is not sensitive enough to detect bio-molecular with ultralow concentrations. To obtain ultrasensitive and stable SERS-active composite, it is necessary to create large specific surface area, in order to attract more target molecules and attain the high plasmonic sensing response.

Recently, hybrid materials gained much attention for their special characteristic in SERS applications [11,12], such as noble metallic nanoparticles combining with graphene or reduced graphene oxide (rGO) or graphene oxide (GO) for their high electrical conductivity, flexibility, chemical stability and the high sensitivity due to specific surface area. The hybrid materials can attract many organic molecules, especially the aromatic group [13]. When the hybrid materials detected R6G, the fluorescence was suppressed by graphene or its derivations and Raman signals were enhanced up to 100 folds [14–16]. Accordingly, it is important to research on graphene combining with Ag/Au hybrid substrates in the application of SERS [17]. The researchers often use the in-situ and self-assembly method to synthesize hybrid structures. The former is a simple and time-saving method, but the particle size and morphology cannot be easily controlled, which would influence the stability. For instance, Liang et al. [18] used ascorbic acid to reduce the $AgNO_3$ in GO solution to fabricate the hybrid substrate and Zhang et al. [19] synchronously reduced $AgNO_3$ and

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GO to the rGO-AgNPs, both of them obtained AgNPs with different size and morphology. Iliut et al. [20] have explored the AuNPs and reduced graphene oxide (Au NPs/rGO) hybrids stabilized with polyvinylpyrrolidone (pvp), however, the loading of Au NPs on rGO sheets was relatively low, which would impact the sensitivity and reproducibility of SERS substrate. The self-assembly is a welcome method to fabricate hybrid structure, because the loading ratio and morphology of the nanoparticles are tunable [21,22].

Therefore, based on a hybrid structure of Au@AgNRs/rGO, we fabricated SERS-active composite with self-assembly method, and obtain a larger active area, stability and more sensitive SERS substrate.

2. Experimental section

2.1. Chemicals

Cetyltrimethylammonium bromide (CTAB), rhodamine-6G, thiram, silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), and tetrachloroauric acid ($HAuCl_4 \cdot 3H_2O$) were purchased from Sigma. Ascorbic acid (AA) was purchased from Bodi Chemical Reagents Co. (Tianjin, China). Milli-Q water (18.2 MÙ cm resistivity) was used for all solution preparations. Glassware was cleaned using aqua regia and washed with deionized water several times before the experiments.

2.2. Synthesis of Au@AgNRs

Au@AgNRs were prepared using a seed-mediated growth method in aqueous solutions [23]. The seed solution was prepared at 25–30 °C. Typically, 0.25 mL of 0.01 M $HAuCl_4$ was added to 7.5 mL of 0.1 M CTAB aqueous solution under vigorous stirring. Following this, fresh ice-cold 0.6 mL of 0.01 M $NaBH_4$ was added. The stirring was stopped until the solution color changed from yellow to brownish. The above-mentioned seed solution was kept at 25 °C temperature for 30 min before using. To prepare the growth solution, 0.3 mL of 0.01 M $AgNO_3$ and 0.32 mL of 0.1 M AA were added to 47.5 mL of 0.1 M CTAB aqueous solution. In the end, 0.1 mL seed solution was added into the as-prepared growth solution. The final solution was stirred for above 40 s and the nanorods were grew at 30 °C for about 13 h under undisturbed situation. The AuNRs were separated with the centrifugal machine for 30 min at 10,000 rpm, and then removed the supernatant.

To synthesize Au@AgNRs, 30 mL of the as-prepared AuNRs solution was centrifuged twice at 10,000 rpm for 30 min and dispersed in 20 mL of deionized water to remove the excess CTAB. Then, the purified AuNRs were added to 40 mL of 0.05 M CTAB aqueous solution under vigorous stirring. After 5 min, 1.3 mL of 0.1 M AA, 1.6–1.8 mL of 0.01 M $AgNO_3$, and 2.4 mL of 0.1 M NaOH were successively added to the above mentioned solution accompanying with vigorous stirring. Lastly, the solution color rapidly changed into wine red within 2 min and Au@AgNRs were formed. To remove the excess CTAB molecules, the as-prepared Au@AgNRs solution was centrifuged consecutively two times at 10,000 rmp for 30 min in our work.

2.3. Fabrication of the rGO-Au@AgNRs and rGO-AuNRs

2.3.1. Synthesis of rGO-Au@Ag/AuNRs

GO was synthesized by the modified Hummers method as described in our previous report [24]. Typically, 14 mL of Au@AgNRs solution was dissolved into GO aqueous solution (6 mL, 1 mg/mL) and ultrasonicated for 30 min, then the solution was transferred into a Teflon-lined stainless steel autoclave and kept at 125 °C for 6 h. When the composite cooled down to room temperature, the blank hydrogel was moved to freeze drying (−60 °C, 8 Pa) until it

became aerogel. Finally, the aerogel was annealed at 600 °C in the flow of Ar gas for 2 h to obtain 3D rGO-Au@AgNRs. The rGO-AuNRs can also be obtained by the same process using 14 mL of AuNRs solution. The AuNRs and Au@AgNRs of the same concentration were investigated as control samples for comparison.

2.4. Raman detection of R6G and thiram

We used R6G and thiram as the probe molecules to investigate SERS activities of rGO-Au@AgNRs. Different SERS substrates have been used for comparison: AuNRs, Au@AgNRs, rGO-AuNRs and rGO-Au@AgNRs. The AuNRs, Au@AgNRs with a volume of 50 μL were deposited on the surface of the quartz glass substrates, separately. Then, 20 μL aqueous R6G (10^{-7} M) was dropped on the above two substrates, subsequently. Similarly, the same volume of R6G was dropped on the as-prepared rGO-AuNRs/rGO-Au@AgNRs. To calculate the EF, the Raman intensity of 0.01 M R6G was compared to the signals on a pure Si wafer.

20 μL thiram solution in ethanol of different concentrations (1.0×10^{-7} to 1.0×10^{-3} M) were dropped on the rGO-Au@AgNRs. Then, they were dried in room temperature environment for SERS detection, respectively. We also detected thiram in the real samples such as real lake water and tap water at a concentration of 1.0×10^{-7} M using the same method.

The Raman spectra were collected under a laser radiation (laser power of 0.17 mW for 532 nm excitation, 50 × objective) with 10 s exposure time and 2 accumulations in a Raman spectrometer (LabRAM HR800, Horiba JobinYvon laser power).

3. Results and discussion

3.1. Composition of Au@AgNRs clung to flexible rGO

The whole fabrication process of the composite rGO-Au@AgNRs is illustrated in Fig. 1. The highly oxygenated GO has lots of sites of negatively charged carboxyl group on the surface [25,26]. In addition, the surface of the Au@AgNRs was positively charged because of CTAB coating on it [27,28]. Therefore, Au@AgNRs could adhere to the surface *via* electrostatic interaction. After a serial of steps as mentioned above, the aerogel was finally annealed to obtain 3D rGO-Au@AgNRs. The CTAB prevents the AuNRs and Au@AgNRs from aggregation but blocks the adsorption of marked molecules onto the AuNR and Au@AgNRs surface. After annealing, the CTAB decomposed and lost its capping, which gave the Au@AgNRs more opportunity to combine with more molecules. We also found that the conductivity of the rGO-Au@AgNRs has been improved by sixty times after annealing (in supporting information Fig. S1). The cooled rGO-Au@AgNRs was then used as a SERS-active substrate, in which quantity of hot spots of Au@AgNRs formed on the rGO, thus it exhibited highly strong SERS activity. Furthermore, rGO-based material is flexible and adjustable in its size and shape to meet its requirements.

3.2. Morphology characterization of Au@AgNRs embedded rGO substrates

The morphology of AuNRs and Au@AgNRs were characterized by a FEI Titan 60–300 transmission electron microscope. As shown in Fig. 2a, AuNRs have fairly unified shapes and sizes with length 32.4 ± 5.1 nm and 14.4 ± 1.9 nm. The various aspect ratios of AuNRs can be obtained by simply changing the proportion of $AgNO_3$. The planar spacing of 0.235 nm in Fig. 2b matches well with the (111) crystal plane of Au. As shown in Fig. 2c and its inset, *i.e.* the HADDF-STEM imaging and EDS-mapping, the Au@AgNRs has a core-shell structure. Because the (200) crystal planes of Au and Ag have nearly