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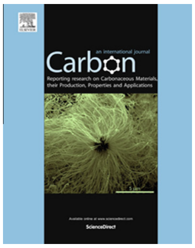

Study on surface-enhanced Raman scattering substrates structured with hybrid Ag nanoparticles and few-layer graphene

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ABSTRACT

We synthesized a set of surface-enhanced Raman scattering (SERS) substrates with hybrid-structures including Ag nanoparticles (AgNPs), AgNPs on top of few-layer graphene (AgNPs-FLG), AgNPs underneath few-layer graphene (FLG-AgNPs), sandwich structure (FLG-AgNPs-FLG) and few-layer graphene (FLG). The experimental results indicate that FLG can effectively protect AgNPs against aerobic oxidation (up to 60 days) and the sandwich structure achieved the best stability (the Raman intensity decreased by only 22.6% at ~1363 cm^{-1}, compared to a 94.03% decrease in the substrate of AgNPs). Besides, the defects of FLG caused the agglomeration of AgNPs and reduced the internal electric field of AgNPs, which ultimately led to a slight increase in the relative standard deviation (RSD) value and a minor decrease in the enhancement factor (EF). By studying local electric field properties of AgNPs and FLG, the principles of the interaction between AgNPs and FLG and also the change of the field and Raman intensity were analyzed theoretically and simulated. Through experiments and theoretical analyses, the hybrid structure of AgNPs and FLG is a potentially valuable and effective way to improve the performance of SERS substrates.

1. Introduction

Surface-enhanced Raman scattering (SERS) was firstly discovered on rough Ag electrode surface by Fleischmann in 1974 [1]. It has shown tremendous potential for many applications, especially bio/chemical molecular analysis at low concentrations, even at single molecule level [2–4]. In order to fabricate SERS substrate with characteristics of high enhancement factor (EF) and high sensitivity, researchers have been working on various SERS substrates in recent 40 years [5–8]. It is well-known that there are two main contributions of the enhancement of Raman signal: electromagnetic (EM) enhancement and chemical (CM) enhancement, and most researches indicate that the EF is mainly provided by EM enhancement excited on rough metal surface [9,10].

Au, Ag and Cu nanoparticles/nanostructures with different morphologies have been investigated to develop efficient SERS platform [11,12]. In these three common noble metal materials, Ag has a higher EF but its chemical instability against oxidation under ambient condition limited its long-term use [13,14]. Therefore, many efforts have been devoted to improve the chemical stability of Ag to avoid oxidation without compromising its SERS sensitivity. The most common approach is to coat Ag nanoparticles (AgNPs) with a

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stable material as a protective layer/shell, such as titania (TiO_2) [15], silica (SiO_2) [16], alumina (Al_2O_3) [16], graphene (GE) and its derivatives [17–20]. In order to achieve full protection of AgNPs without compromising the SERS sensitivity, the main challenge is to prepare a stable, ultrathin and pinhole-free isolating layer/shell. Great efforts have been made to deal with this problem. Synthetic procedures for the formation of TiO_2, SiO_2 or Al_2O_3 layer/shell are not ideal due to difficulty in controlling reaction conditions to obtain an ultrathin protective layer/shell of a few nanometers thick, where strict reaction conditions and long reaction time are required [21]. In contrast, the way to synthesize GE and its derivatives by chemical vapor deposition (CVD) is simpler and more efficient, because one can easily control the thickness of GE layer by adjusting the CVD conditions such as temperature, gas flow and reaction time [22]. For GE/GE derivatives, the enhancement of Raman signal excited by the visible band has been proved to be CM enhancement mechanism [23–25] and the majority of research is focused on the Raman behaviors of GE itself and the composites of GE/GE derivatives for the application of chemical stability for SERS [26,27].

According to the existing problems in current research, this work aims to study the improvement of the stability of SERS substrates (against aerobic oxidation) and the interaction between AgNPs and few-layer graphene (FLG). We prepared SERS substrates in five different structures with a simple, environmental-friendly and low-cost method. Then we compared the effect of the enhancement of Raman signal and the stability, using rhodamine 6G (R6G) as probe molecules. Meanwhile, we used the COMSOL Multiphysics to analyze the local electric field properties in the interaction between AgNPs and FLG to clarify the principles.

2. Experimental

2.1. Synthesis of AgNPs

A simple hydrothermal method of Ag-sol solution was used to synthesize AgNPs [28]. Firstly, 100 mL silver nitrate ($AgNO_3$) solution with a concentration of 1 mM was added to a beaker and placed on a magnetic stirrer. Then the solution was heated to boiling temperature (92 °C ± 4 °C). 1% sodium citrate ($C_6H_5Na_3O_7{\cdot}2H_2O$) of 1 mL was added (the volume of $C_6H_5Na_3O_7{\cdot}2H_2O$ affects the size of AgNPs) while heating and stirring continued. With vigorous stirring the resulting mixture was kept at the boiling temperature for 40 min. Next, the solution was cooled naturally to room temperature. Finally, the Ag-sol solution was sealed, light blocked and stored in refrigerator at 4 °C.

2.2. Preparation of FLG

FLG used in our experiments was synthesized by chemical vapor deposition (CVD) [29,30]. Firstly, Cu foils (25 μm in thickness, purity of 99.8%, purchased from Alfa Aesar) were placed into a Φ80 mm quartz tube inside a tube furnace. Then the quartz tube was vacuumed (2.5 Pa) by a vacuum pump. A mixed gas of hydrogen (H_2) with a flow rate of 30 sccm and argon (Ar) of 500 sccm was filled into quartz tube until the inner pressure of the tube was brought back to atmospheric pressure. While continuously adding the mixed gas, we started to heat the tube with a tube furnace at a heating rate of 50 °C/min until the temperature reached 1000 °C. Then FLG was grown using ethylene (C_2H_4) with a flow rate of 5 sccm as the carbon source under 1000 °C for 10 min. Finally, we closed the output of C_2H_4 and maintained the output of H_2 and Ar until the temperature in the tube was cooled down to room temperature.

2.3. FLG transfer

Polymethylmethacrylate (PMMA, purchased from VIGON Technologies) was firstly spin coated on one side of the Cu foil and cured in a vacuum oven at 120 °C for 3 min. Then the Cu foil with FLG/PMMA film was immersed into ferric chloride ($FeCl_3$) solution with a concentration of 0.1 M until the foil was completely etched away. Next the FLG/PMMA film was washed with deionized water to remove the residual $FeCl_3$ and then transferred onto the substrates. At last, the PMMA layer was removed by acetone and washed with deionized water.

2.4. Preparation of SERS samples

The surfaces of monocrystalline Si substrates (p-type, thickness: 650 ± 10 μm, area: 5×5 mm^2, crystal orientation: $\langle 100 \rangle$, resistivity: 0.01–1 Ω cm, purchased from LIJING Technologies) had been polished before the preparation of SERS samples. We had synthesized SERS substrates in five different structures (shown in Fig. 1): Ag nanoparticles (AgNPs), AgNPs on the top of graphene (AgNPs-FLG), AgNPs underneath graphene (FLG-AgNPs), sandwich structure (FLG-AgNPs-FLG) and FLG on the surface of Si. The preparation steps involved two kinds of modification: Ag-sol solution was dropped onto the surfaces of substrates with spin coating; FLG was transferred onto the surfaces of substrates. Finally, the SERS substrates were washed with deionized water and placed under nitrogen (N_2) until the surfaces had been dried by evaporation.

2.5. Characterization and SERS measurement

The absorption spectrum of Ag-sol solution was examined over the wavelength of 300–800 nm, using an ultraviolet–visible (UV–vis) spectrophotometer (Hitachi High-Tech U-4100). The surface morphologies of the prepared samples were observed by an optical microscope system (Olympus BXFM) and a field emission scanning electron microscopy (FESEM, JEOL JSM-7800F). The thickness of FLG was measured by an atomic force microscopy (AFM, Dimension® Edge™). The results of Ag/O atomic ratio of SERS substrates were confirmed by an energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments X-Max^N). All samples for SERS measurements were prepared by dropping aqueous solution of R6G (10 μL, unless otherwise specified, the default concentration is 10^{-5} M) and dried at 40 °C in N_2. The SERS spectra were acquired with a laser confocal Raman spectrometer (Horbia Jobin Yvon LabRAM HR Evolution) equipped with a 50× objective of numerical aperture (NA) 0.75, at work distance (WD) of 0.37 mm, using an air cooled double-frequency Nd:Yag green