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Original research article

Decoration of Cu films on the microstructural mantis wing as flexible substrates for surface enhanced Raman scattering

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A R T I C L E I N F O

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A B S T R A C T

Noble metal decorated biological materials were applied to surface-enhanced Raman scattering (SERS), which have been widely used in the detection of organic molecules. In this work, a low-cost, environment-friendly and suitable for large-scale production SERS substrate for rhodamine 6G (R6G), 4-aminothiophenol (4-ATP) and crystal violet (CV) detection has been fabricated by depositing copper (Cu) on the surface of mantis wings (MWs) by magnetron sputtering. In the process of preparation, we improved the enhancement effect of the substrate by controlling the sputtering time of Cu. Experiments showed that when the SERS substrate was prepared at the sputtering time of 30 min, the substrate exhibited excellent performance. The SERS performance of the fabricated flexible Cu/MW substrate when employed R6G as probe molecules shows an enhancement factor (EF) of 1.19×10^5 over 10^{-3} M R6G solution. Besides, the prepared SERS substrate exhibits high sensitivity, strong stability and reproducibility. Sensitivity for relatively low R6G concentration (10^{-6} M), 4-ATP concentration (10^{-6} M) and CV (10^{-6} M) were reported.

1. Introduction

Nowadays, surface enhancement Raman scattering (SERS) has been widely used in many fields, such as surface adsorption, chemistry, catalysis, biosensing and medicine [1–6]. SERS technique not only has high sensitivity and selectivity, but also has the advantages of small water interference and nondestructive analysis. Therefore, it presents a great application prospect in the detection of trace substances [7]. With the development of laser technology and material science, the problems of weak SERS signal, poor stability and repeatability of substrate had been solved. Meanwhile, the signal intensity of SERS has been greatly enhanced, the enhancement factor (EF) could reach up to 10^9 and could realize single molecule detection. Preparations of excellent substrates have been one of the greatest challenges for enhancing SERS intensity. Most people focus on the SERS substrate such as noble metals (Au, Ag, Gu) [8–12], and semiconductor materials [13–18]. A variety of techniques has been used to fabricate SERS substrates with good enhancement factors [19–21].

SERS is a method to enhance the Raman scattering signal by adsorbing the molecules on the surface of the nanoscale metal. It also has been shown that the SERS substrate can produce strong SERS signals, mainly because of the strong coupling of local surface plasma resonances (LSPR) at metal nanorough surface leading to local electromagnetic enhancement (“hot spot” areas) [22–24].

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Because the LSPR of gold (Au), silver (Ag), and copper (Cu) are in the range of visible and near infrared wavelengths [25,26], they are often used to make the SERS substrates. But researchers have less research on nanostructured Cu because its chemical properties are unstable and the SERS signal is weak compared to gold and silver [27]. However, due to the low cost, high SERS activity, and strong chemisorption for most analytes, Cu still has great application prospects in the field of SERS [28]. Therefore, Cu was chosen as a noble metal material for the preparation of low-cost, high performance SERS substrates. What is important, however, is that the selection of the substrate materials is important to enhance Raman signal. In the selection of substrate materials, most researchers tended to the materials which have regular surface structure [29,30]. Some researchers, however, has found that the noble metals were modified to some surfaces of natural biomaterials with special structures, and the ideal SERS signal could be obtained. For example, Guo et al. decorated the silver nanoparticles on the surface of cicadas wings by chemical deposition, they got a green, low cost, efficient SERS substrate [29]. By depositing gold nanoparticles on the cicadas wings, a large-scale and low-cost SERS substrate was obtained by Lv et al. [31]. Some researchers who got the ideal SERS substrate by modifying the butterfly wings [32] and dragonfly wings [33], also obtained better enhancement effect.

In this study, we found that the surface of the mantis wings (MW) is covered by a large number of flaky structures, which are disorderly and irregular and have no specific shapes. We deposited Cu onto the surface of the MW by magnetron sputtering system to obtain a low-cost and environment-friendly SERS substrate. In this process, we mainly controlled the thickness of the copper film by controlling the sputtering time to obtain the optimal substrate. In addition, MW, as a pure biomaterials, has the advantages of cheap, flexible, hydrophobic and easily-obtained, and so on. It is found that the super hydrophobic structure and rough surface of biomaterials can effectively reduce the detection limit and achieve low concentration detection. Even if the concentration of the analyte is very low, it can also be successfully detected [34]. The irregular, rough and super hydrophobic surface structure of the MW lets it be the ideal material for the SERS substrate. We know that the traditional method of chemical deposition, which easy to occur aggregation phenomenon, and lithography is expensive and it is not suitable for large-scale production [35]. Magnetron sputtering technique is an ideal physical method. It has many advantages, such as low-cost, low-damaged and simple operation. In SERS detection, we used R6G as a probe molecule. The experiment shows that when the sputtering time was 30 min, the best enhancement effect was obtained. At this time, the EF reached 1.19×10^5 over 10^{-3} M R6G solution, and the detection limit for R6G, 4-ATP and CV was up to 10^{-6} M.

2. Experimental

2.1. Materials and instruments

The MWs were purchased from Beijing Jiaying Grand Life Sciences Co., Ltd. Experiments with mantis wings complied with the accepted ethical standards and were approved by the Ethical Review Board of Yanshan University on 15 January 2018. The Cu (99.99%) target material was obtained from Nanchang Material Technology Co., Ltd. Both R6G, 4-ATP and CV were got from J&K Scientific LTD. The MWs were deposited by Cu nanoparticle with direct-current (DC) magnetron sputtering instrument(JGP450). The surface structure information of MW and Cu/MW were got by scanning electron microscope (Hitachi S-4800 II). The Raman spectra was obtained from Raman system (inVia). The water used in the experiment was ultrapure water, which was acquired from Key Laboratory for Microstructural Material Physics of Hebei Province.

2.2. Sample preparation

MWs were cut into small pieces of 6 mm × 6 mm. These MWs cleaned with acetone, ethanol and ultrapure water for 20 min, and then naturally dried at room temperature. Then the washed wings were fixed on the aluminum sheet before magnetron sputtering. In the process of magnetron sputtering, we controlled the power in 60 W, and the pressure was controlled in 2 Pa. In order to screen out the best sputtering time, we control the sputtering time of 10 min, 20 min, 30 min and 40 min respectively, conformably, we named them as Cu/MW-10, Cu/MW-20, Cu/MW-30 and Cu/MW-40, respectively. In order to prevent Cu from being oxidized, we kept the prepared SERS substrates in the sealed container.

2.3. SERS measurements

The R6G solution with the concentration of 10^{-3} M was prepared by ultrapure water. Then it was diluted to the concentration of 10^{-4}–10^{-6} M. First, we used the 10^{-3} M R6G to find the substrate with best enhancement effect. Then we added 10^{-4}-10^{-6} M R6G on the best substrate to perform Raman detection to determine the detection limit for R6G. Finally, in order to prove the practicability of the substrate, we detected the 4-ATP and CV with concentration gradient of 10^{-3}–10^{-6} M. All of the Raman signals were obtained at room temperature. In the Raman detection, we used the excitation wavelength of 532 nm. The incident power was 0.05 mW. In addition, the recording time of each Raman spectrum was 10 s, and with the spectral resolution of 1 cm^{-1}. In order to reduce the experimental error, we measured ten groups of data each time, and then selected the best one from the ten groups.