A Simple Route for the Preparation of Gold Nanofilms and Their Application in SERS Detection of Pyrene in Water

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Abstract. Design and preparation of various rational gold nanostructures has been recognized as a promising solution for the surface-enhanced Raman scattering (SERS) signal amplification. Here, a simple fabrication method was reported for the synthesis of highly sensitive gold nanofilms for SERS detection through covering ginger-like gold nanoparticles on the stainless steel sheet. The prepared gold nanofilms were then tested by a dip-SPME-SERS method for detecting pyrene. The limit of detection for pyrene standard solution was 0.1 ppb, while the limit of detection for pyrene in tap water and lake water without any pretreatment was 5 ppb, respectively. The whole analysis process takes less than 15 minutes. Our method may be a potential alternative way to the chromatography method. The fabricated gold nanofilms are expected to be used for the rapid and sensitive detection of other pollutants such as organic pesticides and polycyclic aromatic hydrocarbon.

1. Introduction
In recent years, surface enhanced Raman spectroscopy (SERS) has been developed as a very important analytical method, which has been widely used in environmental monitoring, food, biomedicine, criminal investigation and other fields because of its ultra-high sensitivity, high selectivity, fast, real-time detection and nondestructive analysis[1, 2]. So far, researchers have prepared various SERS substrates coated with gold or silver nanoparticles[3, 4]. For example, the SERS substrate was prepared by fixing the gold nanoparticle layer on the metal film coated porous silicon (PSI) [5]. The gold nanoparticles have ever been modified by hydrophobic porous glycidyl methacrylate vinyl dimethacrylate to prepare polymer substrate, which was used to analyze polycyclic aromatic hydrocarbons in water [6].

At present, the preparation methods of gold nanofilms mainly include vacuum evaporation, laser ablation, electrochemical activation and layer by layer chemical reaction[7-9], but the operation process is complex, the cost is high and the speed is slow. Therefore, a more simple and effective approach needs to be developed to overcome these shortages.

In this study, we developed a simple and sensitive dip-SPME-SERS way to detect pyrene in water samples using a gold nanoparticle-coated nanofilm. The substrate is prepared by chemical etching and coating methods[7]. In addition, the characterization of the fabricated gold nanoparticle-coated nanofilm and their performance in dip-SPME-SERS methods were investigated by detect pyrene in water (i.e. tap water and lake water). This method is simple, rapid and low-cost, so it has great development prospects in expanding to a large number of rapid detection of other toxic and harmful residues in food samples.
2. Materials and Methods

2.1 Materials
Chloroauric acid (HAuCl₄·3H₂O) was purchased from Sinopharm Chemical Reagent (Shanghai, China); Analytical standard grade pyrene (97%), hydrochloric acid, methanol (99.5%) and acetone (99.5 %) were purchased from Aladdin Biochemical Technology (Shanghai, China); the stainless steel sheet (304) was purchased from Wuxi Wanxin metal products (Jiangsu, China); the tap water is taken from the local area (Nanchang, Jiangxi).

Other instruments used are as follows: DXR2 laser micro confocal Raman spectrometer (Thermo Fisher Scientific, USA.), SU8010 field emission scanning electron microscope (Hitachi, Japan).

2.2 Preparation of Gold Nanoparticle-coated Nanofilm.
The stainless steel sheet (0.3 cm◊0.3 cm) was washed with distilled water and acetone in an ultrasonic bath (5 min each), dried, and then soaked in concentrated hydrochloric acid in water bath (60 °C) for 15 min. The stainless steel sheet was then washed and dried again with methanol and distilled water (5 min each) in an ultrasonic bath. The cleaned stainless steel sheet was then dipped in HAuCl₄ solution (0.075%, w/w) to form gold nanoparticles on the their surface. The morphological characteristics of the samples were investigated by microscopes and field emission scanning electron microscope (SEM).

As shown in Figure 1, it is the preparation of gold nanoparticle-coated nanofilm and the detection process of pyrene.

2.3 Detection of Pesticides Using Dip-SPME Methods.
Pyrene stock solution of 100 mg/L (100 ppm) was prepared with methanol, then it was further diluted to the desired concentrations (100 to 0.1 ppb) with methanol or tap water before use. The gold nanoparticle-coated nanofilm was dipped in 2 mL of sample solution for 15 min at room temperature. The gold nanoparticle-coated nanofilm was then air-dried and measured using Raman microscopy.

2.4 SERS Measurement.
In this study, the Raman spectra of pyrene standard solutions or tap water doped with pyrene were obtained using a DXR microscopy Raman spectrometer (785 nm, 5 mw). The SERS spectra of the test samples were collected using a 50x confocal microscope objective, a slit width of 25 μm and an exposure time of 2 s.

![Figure 1. Schematic illustration of gold nanoparticle-coated nanofilm fabrication and detection of pyrene](image-url)
3. Results and Discussion

3.1 Fabrication and Characterization of Nanofilm Substrate.

As shown in Figure 2a-b, the surface of the gold nanoparticle-coated nanofilm substrate prepared before and after chemical etching is rough. After immersion in HAuCl₄ solution, the coated stainless steel sheet was golden, indicating that Au was successfully adhered (Figure 2c). Under SEM, there are many ginger like particles evenly and densely distributed on the surface of stainless steel sheet to form a nano film (Figure 2d and Figure 2e). This preparation method is a very simple way to coat gold nanoparticles onto stainless steel sheets. Ginger liked gold nanoparticles may provide amounts of “hotspots”, which has been proved to be very beneficial for Raman spectroscopy [7].

After the preparation of gold nanoparticle-coated nanofilm, its SERS activity and extraction efficiency were detected in 2 ppm of pyrene methanol solution with dip-SPME methods. As can be seen in Figure 3A, between 400 and 2000 cm⁻¹ Raman shift, the gold nanoparticle-coated nanofilm has minimal background noise and does not interfere with the pyrene signal.

In practical application, the stability and uniformity of substrate in SERS technology is very key[10]. To evaluate the uniformity of the substrate, SERS spectra of 10 ppm pyrene were collected from 15 random position on the same substrate (Figure 3B). The peak shape and peak strength were basically consistent, indicating that the substrate enhancement effect has good reproducibility. The relative standard deviation (RSD) of SERS intensity of characteristic peak at 589 cm⁻¹ was as low as 4.53% (Figure 3C), which indicated that the substrate was relative uniformity.

![Figure 2. Before the corrosion of stainless steel sheet by concentrated hydrochloric acid (a), after the corrosion of stainless steel sheet by concentrated hydrochloric acid (b), the gold nanofilm (c) obtained by soaking chlorauric acid, the SEM images of the gold nanofilm at 5000 times (d), and the SEM photos of the gold nanofilm at 30000 times (e).](image-url)
Figure 3. Typical SERS and molecular structure of pyrene
(A), SERS spectra of pyrene measured at 15 substrates (B), Raman intensity of pyrene at 589 cm\(^{-1}\) at 15 locations in the same basement (C).

3.2 Spectral Features of Pyrene
The typical Raman spectrum and molecular structure of pyrene are shown in Figure 3A. There are four most stronger peaks of pyrene on 589, 1228, 1393 and 1605 cm\(^{-1}\) observed (Figure 3A). The peak at 589 cm\(^{-1}\) is related to skeletal stretching, which is used for further characteristic analysis, owing to its strongest intensity. The peaks at 1228, 1393 and 1605 cm\(^{-1}\) are attributed to CH in-plane bending vibration, benzene ring bending vibration and C-C stretching vibration, respectively [11, 12].

3.3 Determination of Pyrene Standard Solutions
In order to study the effect of dip time on the enhancement effect of gold nanoparticle-coated nanofilm as SERS substrate, the Raman spectra of pyrene in standard solutions at different dip time (from 1 min to 60 min) were detected (Figure 4A). The SERS signal of pyrene was detected after dip-SPME process of 1 min, and the SERS signal increased significantly with the extension of dip time from 1 min to 15 min. However, from 15 min to 60 min, the SERS signal began to decrease slowly. This may be due to the saturation of substrate adsorption. Therefore, 15 min was selected as the dip time for the follow-up test.

As shown in Figure 4B, SERS spectra of pyrene standard solutions with different concentrations (0.1 ppb to 100 ppb). The intensities of characteristic peak decreases with the decrease of pyrene concentration. Due to the physical adsorption between the substrate and pyrene, the structure of pyrene does not change significantly when it is adsorbed on the surface of gold nanoparticle-coated nanofilm [13]. Therefore, compared with the conventional Raman spectrum of pyrene (Figure 3A), the SERS spectrum has no obvious shift change [13]. There was a linear regression relationship between pyrene concentration (0.1 to 10 ppb) and SERS intensity of the 589 cm\(^{-1}\) peak (Figure 4C). The regression curve equation is \(y = 73.312 \times + 233.18\), and pyrene concentration and Raman intensity present a nice linear relation with coefficient of determination (R\(^2\)) of 0.9856. According to the formula 3.3 δ/S [14], where δ represents the standard deviation of the blank, and represents the slope of the calibration curve. The detection limit of pyrene was calculated to be 0.1 ppb. The lowest detectable concentration was 0.1 ppb (Figure 4B). However, it can be seen from the error bar that the method has large variations and needs further improvement. This variation may be due to the different size and aggregation degree of gold nanoparticles.
3.4 SERS Determination of Pyrene in Water

In order to further illustrate the advantages of gold nanoparticle-coated nanofilm in practical application, the SERS signal of adding 5 ppb pyrene in lake water and tap water was detected by dip-SPME method, as shown in Figure 5. When the gold nanoparticle-coated nanofilm is used as SERS substrate to detect pyrene in complex matrix, compared with the report in [12], the detection limit in water samples is lower, which prove that our method is more sensitive and efficient.

4. Conclusions

In conclusion, A simple wet-chemical route can be developed for the synthesis of gold nanofilm on stainless steel sheet through displacement reaction in aqueous solutions at room temperature. The prepared gold nanofilm was very sensitive in detecting pyrene in complex matrix (i.e. tap water and lake water) by combining dip-SPME with SERS. Compared with the traditional SPME-GC method, our method with gold nanofilm has the advantages of simplicity, good substrate uniformity, less sample preparation and rapid detection. This fabricated gold nanofilm was provides a useful choice for the efficient detection of organic pollutants.
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6. References
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