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High reliable and robust ultrathin-layer gold coating porous silver substrate via galvanic-free deposition for solid phase microextraction coupled with surface enhanced Raman spectroscopy

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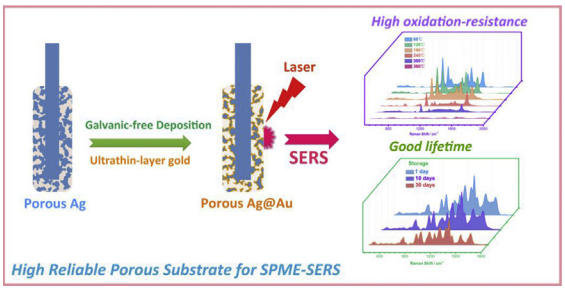
HIGHLIGHTS

- An uniform ultrathin-layer of Au was deposited on porous Ag surface by galvanic-free deposition.
- This coating facilitates to have a high oxidation resistance for the substrate under heating in atmosphere condition.
- A high enhancement factor (1.3×10^6) and low LOD (5.1 ppb) for the extraction and identification of nitrofurazone.
- Rapid detection of prohibited antibiotic and its marker residue in a complex matrix.

GRAPHICAL ABSTRACT



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ABSTRACT

That intense demand for both high sensitivity and high reliability has been a key factor strengthening the surface enhanced Raman spectroscopy (SERS) in the analytical application, particular in the hyphenation with pre-concentration technique. Credible data acquisition and processing is very dependent on the stable and uniform performance of SERS-active substrate. Here, a reliable and uniform ultrathin-layer Au was proposed for protecting the porous Ag fiber (porous Ag@Au) and applied in the solid phase microextraction coupled with SERS. The Au layer was carefully deposited on porous Ag surface to form the uniform film by a galvanic-free displacement reaction. This coating endowed the substrate with high oxidation-resistance under heating and good durability in the atmosphere condition. The extraction and SERS performance of Nitrofurazone and Semicarbazide were investigated on this fiber, the bands at 1350 cm^{-1} and 1387 cm^{-1} were selected as the characteristic peaks for quantitative determination, respectively. This robust and sensitive substrate provide the high enhancement factor of 1.3×10^6 and low LOD of 5.1 ppb for the extraction and identification of Nitrofurazone compounds. Importantly, this work develops a versatile strategy for rapid detection of prohibited antibiotic and its marker residue in a complex matrix.

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1. Introduction

The goal of promoting surface enhanced Raman scattering from an ultra-sensitive spectroscopic technique into a reliable quantitative analytical strategy has attracted the tremendous efforts for many years [1–3]. The challenges are not only how to prepare the sensitive enhancing substrate for the relevant identification, but also the high demand for stability and reproducibility which can provide a valuable vibratory and structural information about the target [4–7]. On the other hand, the substrate capable of robust performance and longer shelf-life may have greater available than just ultra high sensitivity for many applications [8–10]. Currently, the hyphenated technique which coupling solid phase microextraction (SPME) with SERS has been demonstrated as a powerful tool for ultrasensitive analysis, which integrates the preconcentration and Identification in one step rapidly. The SPME-SERS method can be performed using a portable kit of laser spectrometer, it has been successfully applied in the detection of pollutants [11–13], pesticides [14–16] and additive [17,18]. As for this case, the critical question of this technique mainly depends on the intrinsic property of a difunctional substrate, which not only must process the high-efficiency extraction but also the strong SERS response, in particular the uniformity and long-term stability.

Silver is the fascinating and essential material in surface plasmons field. Normally, incident light with compatible momentum can excite surface plasmon polaritons on silver nano crystals interface, which has stronger and sharper local electromagnetic field intensity, and will enhance the inherently weak Raman scattering signal of molecules by many magnitudes [19]. Silver nanostructures substrates are largely preferred for their higher enhancement factor, which promises numerous analytical applications including not only routine detection but also single-molecule mapping and bio-imaging [20–22]. However, the relative activity of silver in the atmosphere leads to the drawback of instability for SERS signals, the sophisticated manipulation is usually needed to be performed carefully to obtain the reliable data. An alternative approach is to protect the Ag nanostructure by a conformal and ultra thin shell from the oxidizing species, such as the coating of Au [23,24], silica [25], alumina [26,27] or alkyl thiol [28,29]. Importantly, Au element is an ideal shell material which will prevent the substrate from oxidation or contamination over a reasonably long period. The ultrathin Au layer exhibit comparable plasmonic properties as silver (local field enhancements) in the longer wavelength range (typically $\lambda > 600$ nm), and significantly improve the surface compatibility of Ag substrate [30,31]. Unfortunately, the deposition of uniform Au layer on the surface of Ag is difficult in the aqueous solution containing Au^{3+}, the galvanic reaction will occur instantaneously between them and corrode the Ag nanostructure [32,33]. In practice, the difference value of work function between the depositing metal with the substrate object dominates whether the monolayer deposition will happen (the work function of Au is larger than Ag, so the Au atom will deposit on Ag atom more difficult than it will deposit onto itself) [34,35]. Hence, the key issues for uniformly depositing is to restrain galvanic replacement and decelerate the deposition rate [36,37]. Many methods have been developed to minimize the galvanic reaction by decreasing the redox potential of Au^{3+} through complexation, such as halide ions [23], sulfite [38], cetyltrimethylammonium bromide [39]. On the other hand, when selecting the appropriate complex agent with an efficient reductant, and controlling the reaction rate, it is demonstrated that the conformal ultrathin layer of Au can be successfully deposited on Ag substrate by chemical method.

Porous silver materials have the good porosity, large specific surface area, excellent mechanical properties, make it very attractive as the substrate materials. The porous silver layer which prepared by conventional electrochemical synthesis can provide an active and clean substrate for potential SPME-SERS application [40,41]. Although the porous silver nanostructure has the greater electromagnetic enhancement for adsorbate, the poor durability still limit their stability and repeatability that is considered as the critical factor for SERS measurement, especially in the complex matrix. In this article, the ultrathin Au layer was deposition on porous Ag surface by the galvanic-free displacement reaction. The galvanic reaction of Ag/An^{3+} was inhibited by regulated the redox potential of Au^{3+} in an alkaline solution containing I^- anion, then Au^{3+} was slowly reduced by ascorbic acid to form the uniform film on Ag surface. The porous Ag@Au substrate was characterized by SEM, EDS, XPS and AFM methods. The stability and uniformity were investigated by SERS using p-aminothiophenol (PATP) as the probe. A robust, reliable and high sensitive Au protecting porous Ag SPME-SERS was successfully fabricated. The SERS response of nitrofurazone (NFZ) and Semicarbazide (SCA) were investigated on this substrate. The extraction capacity was subsequently optimized. Finally, the proposed substrate was applied in the extraction and identification of prohibited antibiotic and its marker residue in seafood, the limit of detection was low to ppb level.

2. Materials and methods

2.1. Chemicals

Nitrofurazone and Semicarbazide hydrochloride as hydrochloride (analytical standards) were purchased from Aladdin chemicals Co. Ltd. p-aminothiophenol (97%), $HAuCl_4 \cdot 4H_2O$, potassium iodide, and ascorbic acid were purchased from Sinopharm Chemical Reagent (China). Silver wire (ø0.4 mm, 99.9%) were obtained from Beijing nonferrous metal research institute. The stock solution was prepared by HPLC grade methanol (TEDIA®), and Milli-Q water (18.2 MΩ) was used in all experiments.

2.2. Preparation and characterization of porous Ag@Au substrate

The porous Ag layer was synthesized by the electrochemical method as the previous articles [14]. A silver wire (effective area ø0.4 × 30 mm) was degreased and washed thoroughly, then employed as a working electrode in the three-electrode system. The porous nanostructure was prepared by cyclic voltammetry scanning from −0.2 V to +0.2 V with the rate of 25 mV/s for 15 cycles at Princeton® PARSTAT 4000 electrochemical workstation, then the prepared fiber was rinsed and dried.

The deposition of ultrathin Au layer on porous Ag was performed by galvanic-free reduction [36]. In a standard synthesis, 50 mL of a mixed solution which has the concentration of 10 mmol L^{-1} NaI and 10 mmol L^{-1} ascorbic acid was added into a beaker in tall form, then the PH value adjusted as 11.0 by 0.1 mL of 0.5 mol L^{-1} NaOH solution. In the beginning, the porous Ag was immersed into this solution via the hanging model, 0.5 mL of 0.1 mmol L^{-1} $HAuCl_4$ solutions was automatically into the system at a rate of 0.05 mL/min under magnetic stirring (300 RMP). After injection, the reaction keep continues for 20 min, then the prepared fiber was rinsed thoroughly with methanol and water.

The crystallinity of porous Ag layer was determined by X-ray diffraction (XRD, Bruker D8 Advance X-ray diffractometer), the morphology of was characterized by scanning electron microscope (JEOL JSM-6700F). The UV-Vis diffuse-reflectance spectra were performed at Shimadzu UV-2550 with integrating sphere. The deposition of Au coating was confirmed by X-ray photoelectron spectroscopy (XPS, ThermoFisher SCIENTIFIC ESCALAB 250) and EDS mapping (Oxford Instruments). The surface topography of Au

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