Surface-enhanced Raman scattering enhancement due to localized surface plasmon resonance coupling between metallic nanoparticles and substrate

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ABSTRACT

In this study, gold nanostructures (AuNSs) and silver nanoparticles (AgNPs) were integrated with a silver micro-flower-like structure deposited on a screen-printed carbon electrode (AgMF-SPCE) for enhancing surface-enhanced Raman scattering (SERS) by using 4-mercaptobenzoic acid (4-MBA) as a Raman reporter. SERS was enhanced by approximately 3.6–52.1-fold, depending on the frequency of the incident laser, the localized surface plasmon resonance frequency of metallic NPs, and particle–particle aggregation effects. Compared with AgNP/SPCE and AgMF-SPCE substrates, the AgNP/AgMF-SPCE substrate showed high temperature tolerance and long-term durability. Furthermore, the proposed substrates easily obtained hot spots for other Raman reporters such as 4-aminothiophenol, 5,5′-dithiobis-2-nitrobenzoic acid, and 4-chlorothiophenol. A linear relationship was found between the Raman signal and the concentration of Raman reporters in the range 10 nM–100 μM, with the limit of detection in the range of 6.19–77.2 nM at a signal-to-noise ratio of 3.0. These results suggest that the AgNP/AgMF-SPCE substrate will be well suited for quantitative analysis.

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1. Introduction

Surface-enhanced Raman scattering (SERS) is well-known for its high sensitivity toward analytes that are adsorbed on roughened surfaces of metals or on the surface of metallic colloids (best on Au or Ag) [1–3]. Through electromagnetic field and chemical enhancement, Raman signals of the adsorbed molecule are often enhanced by a factor of 10^2 to 10^6 [4–6]. Thus, limits of detection (LODs) for small molecules in the range of 10^{-9}–10^{-12} M have been observed, and such limits provide an extremely rapid and highly sensitive technique in chemical/biological sensing, medical diagnostics, and environmental monitoring [7–12]. Up to now, colloidal Au or Ag particles of different shapes and sizes have been widely investigated for developing a highly efficient SERS substrate [13–18]. Flower-like Au and Ag microstructures are particularly attractive, because they possess a characteristic surface roughness that favors the production of a strong electromagnetic field enhancement for SERS [19–24].

Although several sample-handling techniques are employed to collect SERS spectra for analytical quantification of analytes, a simple technique entails the use of a commercial product, Klarite [25]. In this technique, analytes in aqueous solution are adsorbed physically or chemically on the prepared SERS-active substrate by dipping the substrate in the sample solution or adding a drop of sample solution onto the substrate before the substrate is dried in a vacuum dryer and exposed to laser excitation. This technique provides an easy means of obtaining vibrational information about analytes near roughened metallic surfaces. As has been reported, a flower-like Au nanostructure (AuNS) array can be obtained by photolithography and electrodeposition, and its surface roughness can be controlled by the fabrication procedure to yield a highly enhanced SERS signal to detect brilliant cresyl blue, benzenethiol, and adenine with high sensitivity [23]. However, the fabrication of such SERS-active substrates involves a sophisticated lithographic procedure. In another report, Li and coworkers replicated an Au nanoflake film from a self-assembled dipeptide, which has flower-like hierarchical architecture [22]. The enhancement factor (EF) of 4-mercaptobenzoic acid (4-MBA) molecules on the Au nanoflake surface was approximately 10^4. In 2014, Xia and coworkers reported a hierarchical flower-like Ag microstructure achieved through the in situ reduction of Ag^+ ions by using a polyaniline template [21]. The EF of 4-MBA molecules on the flower-like Ag microstructure surface was approximately 10^5. However, these reported methods of producing flower-like Au and Ag microstructures require hard or soft templates, and the preparation procedure is also time- and labor-intensive. An easy, low-cost, and template-free synthesis of desert-rose-like Ag

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mesoparticles directly deposited on a screen-printed carbon electrode (SPCE) substrate through a cyclic voltammetric method has been demonstrated by Lin's group [19,20]. The EF of 4-MBA molecules on the desert-rose-like Ag mesoparticle surface was approximately 1.3×10^5. This SERS-active substrate had high reproducibility, with the relative standard deviations (RSD%) for intraday and interday reproducibility being <4.1% and 6.7%, respectively. However, the drop-coating or dipping method for preparing the samples does not offer an approach to preconcentrate the analyte before analysis.

Another SERS sample-handling method involves selectively adsorbing analytes from aqueous solution by SERS-active metallic nanoparticles (NPs), which are then concentrated through centrifugation and spotted onto a silicon substrate for SERS measurements. An additional advantage of this method is that it allows aggregation of SERS-active metallic NPs and produces stronger enhancement due to the localized surface plasmon resonance (LSPR) coupling between SERS-active metallic NPs [26–30]. Similar to LSPR coupling, the surface of planar substrates, referred to as surface plasmon polariton (SPP), has also been well studied [31–36]. Furthermore, Zheng et al. qualitatively observed LSPR-SPP coupling between silver NPs (AgNPs) and surface plasmons of planar Ag substrates [37]. The Raman scattering for 4-aminobenzenethiol (4-ABT), which was produced from adsorbing 4-ABT on a smooth Ag substrate and spotting AgNPs on it, gained an enhancement comparable to that for 4-ABT adsorbed on an electrochemically roughened Ag substrate. They demonstrated that the SERS enhancement of 4-ABT could result from the electromagnetic coupling between AgNPs and the smooth Ag substrate. To gain a deeper understanding of the SERS behavior, a systematic study of the coupling effect between metallic NPs and a SERS-active substrate, particularly metallic NPs with different morphologies, optical properties, and sizes, is required.

In this study, we focused on quantifying the Raman scattering enhancement and maximizing the SERS intensities by using metallic NPs and a SERS-active substrate. SERS spectra of 4-MBA were acquired to determine the SERS enhancement of AuNSs and AgNPs on an electrochemically deposited Ag micro-flower-like structure on an SPCE (AgMF-SPCE) substrate and to study the effects of the metallic NP morphology, optical property, and size on the SERS intensity of 4-MBA. This paper presents the experimental conditions and the resulting interaction between metallic NPs and the AgMF-SPCE substrate for the SERS detection of 4-MBA using 532-nm excitation. Under optimum conditions, the AgNP/AgMF-SPCE substrate provided high reproducibility, robustness, and durability. The LOD for 4-ABT, 5,5′-dithiobis-2-nitrobenzoic acid (DTNB), and 4-chlorobenzenethiol (4-CBT) was determined using AgNP/AgMF-SPCE substrates. This geometry can serve as a very important analytical tool for assays on 2-D SERS-active substrates.

2. Experimental methods

2.1. Materials

All chemicals, namely silver nitrate, sodium tetrachloroaurate(III) dehydrate, sodium citrate, sodium borohydride, catechin, hydrogen peroxide, 4-MBA, 4-ABT, 2-hydroxyethyl piperazine-1-ethanesulfonic acid (HEPES), sodium hydroxide, and hydrochloric acid, were of ACS grade and purchased from Sigma-Aldrich (Milwaukee, WI, USA). L-ascorbic acid, dimethyl sulfoxide (DMSO), 4-CBT, DTNB, sodium phosphate dibasic, sodium phosphate monobasic, and sodium phosphate were of ACS grade and purchased from Acros Organic (Taichung City, Taiwan, ROC). Sodium phosphate dibasic (1.0 M) and sodium phosphate monobasic (1.0 M) were used to prepare phosphate buffer solution (PBS; 1.0 M; pH 7.4). Ultrapure water from a Milli-Q ultrapure system (Millipore, MA, USA) was used for all the experiments. SPCEs were obtained from Zensor R&D (Taichung City, Taiwan, ROC).

2.2. Preparation of AuNSs and AgNPs

Three different gold nanomaterials were synthesized for this study and are denoted Au-1, Au-2, and Au-3. Au-1 was synthesized by reducing NaAuCl₄ in HEPES buffer [38–40]. Specifically, NaAuCl₄ (20 mM, 5.0 μL) was mixed with HEPES solution (40 mM, 1.0 mL), shaken for 1 min, and then left to grow in size for at least 60 min. After growing, the mixture was purified through centrifugation (RCF 5000 ×g) for 15 min. The pellets were then redispersed in 1.0 mL of ultrapure water and stored at 4 °C. Au-2 was synthesized by mixing NaAuCl₄ (10 mM, 2.0 mL) with ultrapure water (50 mL) in the presence of catechin (0.6 mM) [41]. The mixture was stirred gently at 27 °C for 20 min, at which point the solution color changed from pale yellow to light purple, indicating the formation of Au-2. After another 40 min of stirring, the mixture was purified through centrifugation (RCF 10,620×g) for 10 min. The pellets were then redispersed in 10 mL of ultrapure water and stored at 4 °C. The Au-3 suspensions were prepared as described previously [42]. In brief, a 50-mL aqueous solution containing 4 mM sodium citrate was brought to a vigorous boil with stirring; 200 mM NaAuCl₄ (0.25 mL) was then added rapidly to the solution. The solution was heated for another 8 min, at which point its color changed from pale yellow to deep red. The solution was cooled to room temperature and stored at 4 °C.

The Ag-1 suspensions were prepared through the sodium-citrate- and sodium-borohydride-mediated reduction of silver nitrate [28]. A 20-mL ultrapure water solution was heated to boiling, and then silver nitrate solution (100 mM, 50 μL), sodium citrate solution (100 mM, 50 μL), and sodium borohydride solution (5 mM, 1.2 mL) were added in sequence while stirring. The solution was heated under reflux for an additional 30 min, at which point its color changed from colorless to yellow, indicating the formation of Ag-1. The Ag-1 solution was cooled to room temperature and stored at 4 °C. For simplicity, the concentration of the prepared Ag-1 solution is defined as 1×. The Ag-2 to Ag-5 suspensions were prepared using a seed-mediated method by mixing silver nitrate (2–12 mM, 2.5 mL) and L-ascorbic acid (10 mM, 2 mL) first and then adding them to ultrapure water (4 mL) and sodium citrate (100 mM, 500 μL) with various amounts of Ag-1 solution (1 mL, 0.3–3.3×). After 30 min of stirring, the Ag-2 to Ag-5 solutions were stored at 4 °C.

2.3. Electrochemical synthesis of AgMF-SPCE

According to our previous study, a SERS-active AgMF-SPCE substrate was prepared using cyclic voltammetry, which was carried out with a CHI 6124e electrochemical workstation (CH Instruments, Austin, TX) [19]. The three-electrode system consists of the SPCE as the working electrode (geometric area, 3.14×10^{-6} m²), a Ag/AgCl reference electrode, and a platinum wire auxiliary electrode. Prior to the deposition process, a bare SPCE was preoxidized by applying a potential of 0.5 V for 10 min in 1.0 M PBS at pH 7.4 with continuous stirring. Subsequently, the electrochemical synthesis of the AgMFs on the SPCE substrate was performed by cycling the potential between −0.3 and 0.3 V in 10 mM AgNO₃ aqueous solution containing 300 μL Au-3 suspensions at a scan rate of 2.5 mVs⁻¹ for 15 cycles. After the electrochemical process, the AgMF-SPCE substrate was removed from the solution and rinsed thoroughly with ultrapure water.

2.4. Characterization

A JSM-6510 scanning electron microscope (SEM) (JEOL, Tokyo, Japan) and a JEM 2010 transmission electron microscope (TEM) (JEOL, Tokyo, Japan) were used to measure the morphologies of the prepared AuNSs and AgNPs. Energy-dispersive x-ray spectroscopy (EDS) (Oxford Instruments, Oxfordshire, UK) was used to confirm their compositions. An Evolution 200 UV–vis spectrometer (ThermoFisher, NY, USA) was