Applied Surface Science 283 (2013) 52–57

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Facile preparation of silver nanoparticle films as an efficient surface-enhanced Raman scattering substrate☆

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ARTICLE INFO

Article history:
Received 28 April 2013
Received in revised form 28 May 2013
Accepted 28 May 2013
Available online 12 July 2013

Keywords:
Silver nanoparticles
Ni foam
Seed-mediated growth method
Surface-enhanced Raman scattering (SERS)
Melamine

ABSTRACT

Here, we report a new and facile method to prepare silver nanoparticles (Ag NPs) film for surface-enhanced Raman scattering (SERS)-based sensing. The porous Ni foam was used as a template to generate high quality of Ag NPs by seed-mediated growth of metallic nanoparticles. The preparation process is very economic and environment-friendly, can achieve the recovery of the raw materials. We found that the type of silver-plating solution and the growth time are two key factors to determine the magnitude of SERS signal enhancement. Using rhodamine 6G (R6G) and 4-animothiophenol (4-ATP) as probe molecules, the created Ag NP films exhibited relatively high enhancement ability, good stability, and well reproducibility. The synthesized SERS-active substrate was further used to detect melamine molecules, an illegal additive in infant milk powder, and the limitation of detection can reach 1 μM.

1. Introduction

Since its discovery 30 years ago, surface-enhanced Raman scattering (SERS) has gained much attention due to its superior enhancement ability and potential applications [1–4] in many analysis fields, such as food safety [5,6], environment pollutants [7,8], as well as in life sciences [9,10]. However, SERS still has not gained wide acceptance as a routine analytical tool, attributing to the poor stability and the high cost of SERS substrate, which limits the development of the SERS-based devices.

From the application view, it is urgent to prepare SERS substrate with high enhancement ability, good stability, well reproducible, and low cost. Currently, many periodic arrays of nanoparticles were fabricated by nanosphere lithography [11], electron beam lithography [12], and focused ion beam milling [13]. Nevertheless, these techniques are too technologically demanding and expensive to prepare large quantities of substrates for the practical applications. So, the template methods were developed to construct excellent substrates. Many smart thoughts were reported to construct Ag/Au nanoarrays by the highly ordered porous templates, such as porous silicon [14], and polymer (polyaniline, DNA and protein) network [15–19]. Despite many high sensitive SERS sensors have been fabricated by these methods, their applications were still restricted in the laboratory testing.

Ni foams have been commercially available two decades ago, and they are commonly/frequently used as an important porous material in electrochemistry [20,21]. The properties of Ni foam like high specific surface area, very good mechanical strength and low cost render them as an ideal matrix for fabricating highly efficient SERS substrate. Most of the time, silver nanostructures is preferred to fabricate SERS substrate since it provides a higher SERS enhancement efficiency in the visible light wavelength region than Au or other metals. Researchers have prepared Ni nanowires and nanocarpets as templates to construct Au film for SERS detections [22]. The obtained substrates were reusable and quite active in SERS enhancement, but the preparing steps for templates are still complex.

In this paper, we used Ni foam as the template to prepare Ag NPs for SERS by expanding the seed-mediated growth to the fabrication process. Ag seeds were formed directly on the Ni foam by the photoreduction of Ag^+ ions. These synthesized Ag seeds grow up to Ag NPs in the silver-plating solution. Several experimental parameters for the optimized creation of Ag NP films were investigated. We utilized these Ag NP films as SERS substrate for

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http://dx.doi.org/10.1016/j.apsusc.2013.05.154

R6G, 4-ATP, and melamine sensing. The SERS experiments indicate that our Ni foam-based Ag NP films have relatively high sensitivity, good reproducibility and stability for the sensing of different molecules. It should be noted that, this preparation process is very economic and environment-friendly. The Ni foam can be recovered by simple dipping in nitric acid solution, and the $AgNO_3$ obtained in the solution still can be used to prepare Ag NP films on Ni foam.

2. Experimental

2.1. Materials

Ni foam was purchased from Changsha Lyrun New Materials Co., Ltd. (Changsha, China). Silver nitrate was obtained from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). Sodium hydroxide, ammonia, D-glucose, potassium sodium tartrate, sodium citrate, potassium hydroxide, ethanol were obtained from Beijing Chemical Works (Beijing, China). Rhodamine 6G (R6G) was purchased from Exciton Chemical Co. Inc. (Dayton, OH). 4-Aminothiophenol (4-ATP) was purchased from Alfa-Aesar. Melamine was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were used as received. Glassware were cleaned in aqua regia (Caution: very corrosive liquid) and rinsed with deionized water thoroughly. Ultrapure water (18.2 MΩ cm, produced by a Milli-Q system) was used throughout this work except for special indication.

2.2. Formation of Ag seeds on Ni foam

The Ni foam was immersed into 3 mL of 0.05 M $AgNO_3$, and was illuminated with UV light ($\lambda = 265$ nm) for 10 min. The immersion and illumination step was repeated and the foam was then illuminated for 30 min to grow tiny Ag seeds on the backbone of Ni foam.

2.3. Preparation of Ag NP films by seed-mediated growth

Two approaches were developed to prepare the AgNPs films. For route 1, the Ag seed-covered Ni foam was placed into the solution containing 60 mL of 37 mM silver ammonia $Ag(NH_3)_2^+$ and 50 mM D-glucose. The reaction was performed under 5 °C for specific time to produce Ag NP films [14]. For route 2, Ni foam was immersed into 50 mL solution of 60 mM silver ammonia $Ag(NH_3)_2^+$ and 180 mM potassium sodium tartrate, and reacted at room temperature [23]. After the reactions were completed, these substrates were washed with ultrapure water, dried with nitrogen flow and then used as SERS substrates.

For contrast, citrated-capped Ag NPs were prepared according to previously reported method [24], and 30 μL of the prepared Ag sol was dropped onto glass slide to prepare a SERS substrate.

2.4. Instrumentation

SERS spectra were collected using a Renishaw 2000 model confocal microscopy Raman spectrometer with a CCD detector and a holographic notch filter (Renishaw Ltd., Gloucestershire, UK). Radiation with a wavelength of 514.5 nm produced by an air-cooled argon ion laser was used for the SERS excitation. The spectra were collected using a 20× microscope objective (N.A. = 0.4) with 100% amplitude of 12 mW laser power and 10 s data acquisition time. All the substrates were incubated in probe molecule solutions for 1 h. The morphologies and energy dispersion X-ray (EDX) analysis were obtained by FEI/Philips XL30 ESEM FEG field-emission scanning electron microscope (SEM).

3. Results and discussion

3.1. Preparation of Ag NPs on Ni foam

The Ni foams employed in the research were commercial products with a thickness of 1.8 mm. SEM was used to characterize their structures. Fig. 1 shows the surface morphology and microstructure of the Ni foam and the as-prepared Ag NPs on Ni foam. In Fig. 1a, it can be observed that the Ni foam has three dimensional, porous and cross-linked grid structure. There are many open pores, mainly pentagonal in shape with two dominant pore size, about 200 ± 100 μm and 600 ± 200 μm, respectively. Fig. 1b and c displays the Ag NPs have grown on the surface of the Ni foam by route 1. The seed-mediated growth process was reported by Jana et al. [25], larger monodispersed nanoparticles can be prepared from the growth of metallic seeds [26]. Dense Ag NPs with a size 10–60 nm are observed in Fig. 1c, which is in the range of 10–100 nm size suited for SERS detection [27]. Fig. 1d and e gives the morphology of Ag NPs prepared by route 2. The size of Ag NPs distributed in a wide range, from tens to hundreds nanometers, which decrease the uniformity of the whole substrate. The Ag NPs thin film in Fig. 1c was characterized by EDX to get its structural information, as shown in Fig. 1f. The EDX confirmed that the samples consist of element Ni and Ag. The signal of Ni is ascribed to Ni foam. The Ag signal results from the Ag NPs deposited on the backbone of Ni foam. No other signals were observed in the EDX, indicating that the as-prepared sample is pure.

3.2. Optimization of experimental conditions

The type of silver-plating solution and the growth time are two key factors to influence the magnitude of SERS signal enhancement and the sensitivity. How to optimize the substrates became an important task for achieving high sensitive detection by SERS. The R6G molecule was chosen as the probe molecule due to its large Raman scattering cross section and well-established Raman spectral information [28].

The selection of growth method: to determine the influence of silver-plating solution on the SERS performance, two kinds of silver-plating solution were selected to deposit the Ag NP thin film. The obtained two substrates were immersed into 500 nM R6G solution for 1 h. Fig. 2 shows the SERS spectra of R6G molecules on the bare Ni foam (Fig. 2a) and two created substrates (Fig. 2b and c). It can be found that the intensity of SERS bands in curve c were much higher than that in curve b. The SERS signal intensity at 1650 cm^{-1} on sample of route 1 is about three times as that obtained from the samples of route 2. It is proved that route 1 is better than route 2 to prepare SERS substrates.

The selection of growth time: the morphologies of the Ag NPs are strongly depended on the growth time. We chose 2, 5, 8 min as growth time, and the obtained substrates showed different enhancement ability, as exhibited in Fig. 3. It can be found that as the growth time increased, the enhancement ability also increased. Further increase the growth time, such as 10 min, led to enhanced SERS signal, but the uniformity of substrate and reproducibility of SERS signals were not good due to the heavy aggregation of Ag NPs. So the best performance was given on 8 min prepared substrate.

Based on the above experiments, we chose route 1 with 8 min growth time as the optimal experimental conditions for preparing Ag thin film for SERS.

3.3. SERS properties of Ag NP film on Ni foam

The first important element to a new SERS-active substrate is the sensitivity. Yang's group had done many excellent works on designing the high sensitive SERS sensors [15,29–32]. For instance, they