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Research paper

Space confined electroless deposition of silver nanoparticles for highly-uniform SERS detection

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ABSTRACT

We demonstrate an efficient method to improve the reproducibility of SERS detection by controlling the distribution of silver nanoparticles (AgNPs) using Si nanopillar arrays as space confined templates for generating AgNPs with electroless deposition. In the detection of 4-MPy, the relative standard deviation of SERS intensity is decreased to ca. 5.27% from 23.2% by using the AgNPs selectively deposited on Si nanopillar array instead of that randomly deposited on blank Si. Moreover, the SERS-active substrate has good performance in detecting milk contaminated by melamine. This method could be used in real detection.

1. Introduction

Surface-enhanced Raman scattering (SERS) is an attractive label-free analytical technique because of its high sensitivity, which is widely used in the fields of chemical analysis, environment monitoring and food safety [1–3]. Sensitivity and reproducibility are two key factors for the SERS detection [4,5]. Since discovered by M. Fleischmann, a large variety of SERS substrates based on noble metal nanostructures or nanoparticles have been reported [6]. SERS substrates based on nanoparticles have been widely used for their low-cost and high-throughput, which are usually created by assembly and in-situ deposition [7,8]. For the assembly methods, the metal nanoparticles are synthesized in solution and then assembled onto the prepared substrates [9,10]. The size and the type of nanoparticles can be controlled by tuning the synthesis condition [9,11,12]. The prepared substrates could perform high sensitivity in SERS detection, sometimes even down to nanomole level [13]. However, it is difficult to precisely control the gaps between adjacent nanoparticles [12]. The deviation in the gaps could lead to a poor reproducibility in SERS measurements [14]. Moreover, the organic ligands coated on AgNPs may introduce unexpected Raman signals, which also could lower the reproducibility in SERS detection. The effect of organic ligands can be avoided by taking in-situ electrochemical deposition and electroless metal deposition method (EMD), which are based on replacement reaction on substrate [15]. The AgNPs are directly formed on the substrate without the need for any organic ligands [16]. However, the random distribution and the different sizes of the AgNPs on a blank substrate will result in a lower reproducibility in SERS measurements [17]. Therefore, to improve the uniformity of AgNPs is one of the most important approaches for increasing the reproducibility of SERS measurements [16]. In our previous work, we found that the morphology of AgNPs generated by in-situ deposition could be confined using a patterned substrate [18]. However, how to improve the reproducibility in SERS measurements by confining the space of AgNPs with EMD is still less addressed.

Herein, we present a space confined method to control the distribution of AgNPs by using Si nanopillar array as template for EMD process. The AgNPs are selectively deposited on the top surface of Si nanopillars. The space of AgNPs is more uniform than that deposited on blank Si substrate because the reduction reaction is confined into a small area. The size and gap of the AgNPs can be varied by adjusting deposition time, which is vital to the localized surface plasmon resonance (LSPR) and SERS enhancement. The AgNPs on Si nanopillars (AgNPs@Si-nanopillar) show stronger signal with lower deviation than the AgNPs on blank Si (AgNPs@Si). With the optimized deposition time, the SERS enhancement of AgNPs@Si-nanopillar arrays is 2.2×10^6. Meanwhile, the relative standard deviation (RSD) of SERS intensity is decreased to ca. 5.27% from 23.2% by using AgNPs@Si-nanopillars as substrate instead of AgNPs@Si. The AgNPs@Si-nanopillar arrays can be used to detect

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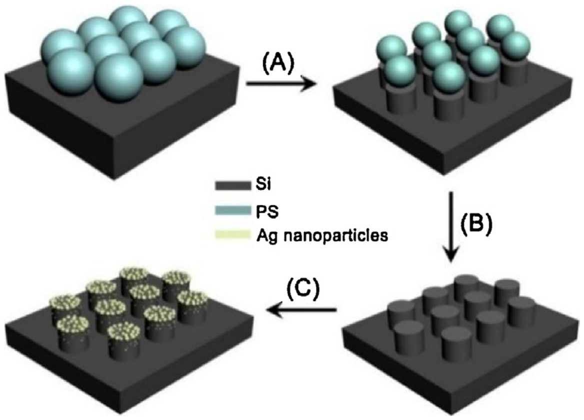

Fig. 1. Strategy for fabricating AgNPs@Si-nanopillars. (A) Fabricate Si nanopillar array by taking RIE process; (B) Remove residual PS nanospheres by taking an ultrasonic bath of tetrahydrofuran; (C) Conduct EMD process by immersing Si nanopillars in the reaction solution containing 5 mM silver nitrate and 11.5 mM hydrofluoric acid to form AgNPs.

low concentration melamine in milk. This method may provide an alternative approach for preparing SERS-active substrates with good reproducibility and can be used in food safety detection.

2. Experimental

2.1. Materials

The monodispersed 538 nm polystyrene (PS) spheres with less than 5% diameter variation were obtained from Sphere Scientific Co., Ltd. Wuhan, China. 4-mercaptopyridine (4-MPy, powder) was obtained from Sigma-Aldrich. One-side polished n-type (100) oriented Si wafers with a resistivity of 0.008–0.02 Ω/cm were purchased from GRINM Advanced Materials Co., Ltd. Beijing, China.

2.2. Fabrication of Si nanopillars

The monolayers of PS nanospheres were initially assembled on the pretreated Si substrates according the method reported elsewhere [19]. And then the reactive ion etching (RIE) process was conducted to fabricate Si nanopillars on a Plasmalab 80 Plus (ICP65) system (Oxford Instruments Co., UK) (Fig. 1A). After the RIE process, the residual PS nanospheres were removed by taking an ultrasonic bath of tetrahydrofuran, ethanol and deionized water for 5 min consecutively (Fig. 1B).

The condition for reducing the size of PS nanospheres was carried out in a flow of O_2 (20 sccm) with a RF power of 30 W, an ICP power of 30 W under the pressure of 40 mTorr. The condition for etching Si substrate was carried out in a flow of SF_6/CHF_3 (6/45 sccm) with a RF power of 25 W, an ICP power of 100 W under the pressure of 8 mTorr. The etching time for reducing the size of PS nanospheres and etching Si was set at 11 and 2 min, respectively.

2.3. Electroless deposition of AgNPs on Si pillars

The 10 mM $AgNO_3$solution and 23 mM HF solution were prepared separately. They were mixed just before the depositing process. The patterned substrate was immersed in the reaction solution containing 5 mM $AgNO_3$ and 11.5 mM HF to form AgNPs. After a certain time, the substrate was took out and rinsed with deionized water, and then dried with flow nitrogen (Fig. 1C). In the EMD process, Si substrate acts as the reduction agent to provide electrons to silver ion for the formation of AgNPs [20].

2.4. Characterization

The diameter and area percentage of AgNPs were calculated by using NanoMeasure and Image J software, respectively. The morphological characterization was carried out by scanning electron microscope (SEM, HITACHI SU8020 field emission scanning electron microscope). The reflective spectra were recorded on an R1-A-UV series spectroscopy meter (Shanghai Idea optics Technology Co., Ltd, China). The samples for SERS detection were prepared by immersing the substrates in a 10^{-5} M 4-MPy ethanol solution for 1 h. Then the samples were rinsed with ethanol and deionized water, followed by drying with flow nitrogen to remove the unbound 4-MPy molecules. The SERS spectra were collected using an optical fiber portable Raman spectrometer (B&W Tek Inc.) with an excitation wavelength of 532 nm and a laser power of 4.7 mW. The Raman signal integration time was 5 s.

3. Results and discussion

Si nanopillar arrays with different parameter were prepared under the given RIE condition with different etching time. The Si nanopillar array with a diameter of 360 nm and height of 217 nm (Fig. 2A) was chosen as the template for the deposition of AgNPs. We investigated the effect of deposition time on the morphology of AgNPs@Si-nanopillars by extending the deposition time from 15 to 150 s at intervals of 15 s. The images of AgNPs@Si-nanopillar arrays of the typical deposition step are given in Fig. 2B–D with the deposition time of 15, 75 and 150 s. The AgNPs@Si-nanopillar arrays fabricated with other deposition time are also recorded with SEM images and shown in Fig. S1. At the beginning of the deposition process, most of the AgNPs are formed around the edge of Si nanopillars (Fig. 2B) because the density of surface energy at the edge is higher than that on the flat surface [21]. The nanopillars provide an active area for the EMD. As extending the deposition time (Fig. 2C), the AgNPs grow bigger and some AgNPs start to form on the center of nanopillar top surface. When the deposition time is further extended to 150 s (Fig. 2D), some of the AgNPs on the adjacent nanopillars connect to each other. The correlation of the average diameter of AgNPs and the deposition time is plotted in Fig. 2E. The black and white histograms indicate the average diameter of AgNPs deposited on blank Si and Si nanopillars, respectively. With increasing the deposition time, the average diameter increases gradually from 37 to 91 nm and the variation decreases as shown with the error bars in Fig. 2E. The size deviation of AgNPs on nanopillar and flat Si is less than 10 nm with the same deposition time. The detailed diameter distribution of AgNPs@Si-nanopillars is shown in Fig. S2 and fit to Gaussian curve. As shown in Fig. 2F, the sigma values of Gaussian curve for AgNPs@Si-nanopillars are evidently smaller than that for AgNPs@Si, which indicates the size and shape of the AgNPs on Si nanopillar array are more uniform than on flat Si. Particularly, the average diameters from different substrates are nearly the same with the same deposition time, but the sigma values for AgNPs@Si-nanopillars are decreased by ca. 23.7% comparing with that for AgNPs@Si. In addition, the average interparticle distance is smaller for AgNPs@Si-nanopillar. Here we believe the nanopillars serve as the template for site selective deposition due to the higher density of surface energy on their top surface. Meanwhile, the fluoride produced by CF_x radicals polymerization during the RIE process located ontheside wall of Si nanopillars decreases the density of surface energy [22]. This makes the AgNPs prefer to form on the top surface of the Si nanopillars. So only a few of small AgNPs are formed on the side wall of nanopillars compared with the top surface of nanopillars, which can be seen in the cross-sectional SEM images in Fig. S3. The substrate is divided by the nanopillars