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Synthesis of the 3D AgNF/AgNP arrays for the paper-based surface enhancement Raman scattering application

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ABSTRACT

Paper-based SERS sensor has attracted considerable attention recently, resulting from the separation, aggregation and high sensitive detection of biomolecules. However, optical losses, caused by the holes or "vase"-like defects, affect the overall intensity of the electromagnetic (EM) coupling and then the Raman signal. Silver nanoflowers (AgNFs) connected with silver nanoparticles (AgNPs) arrays are proposed and firstly obtained onto such "vase" surface to enhance the EM coupling. AgNFs are easily self-assembled on the defects, and the closed packed AgNPs can be formed on the other area. Multiple cascaded amplification mechanisms (localized surface plasmon mode and optical standing waves or refraction) are used to promote the EM magnification. Such paper card is also exploited successfully as an integrated platform, allowing for ultra-sensitivity (1×10^{-19}M) CV and (1×10^{-20}M) R6G detection.

1. Introduction

Surface-enhanced Raman spectroscopy (SERS), a label-free surface-sensitive technique with its increased sensitivity, cost efficiency and simplicity, has drawn great attention to detect pollutants [1], pesticides [2], antibiotics [3] and illegal additives [4]. In order to utilize the SERS technique to extract the individual component spectral from that of a mixture, separation of the various molecules should be done firstly. This is caused by the abundance of inevitable distortion, overlap and tail of SERS spectra and molecular deformation caused by metal–molecule interactions on the mixture detection. Integrating SERS detection with separation capability into a single sensing system is one of the feasible strategies to solve the problem, where SERS was used as a readout method after separation [5].

Paper with the inherent ability of separating the mixtures, due to capillary-action fluidic [6,7], has been developed to achieve the combination with noble metal nanostructures as new fashioned and multifunctional SERS substrates. Various paper (such as filter paper [8–12] photocopy paper [13] and cellulose paper [14,15]) and fabrication methods (such as soaking [16–18], inkjet printing [19,20], screening printing [21,22], filtration [23,24] and in situ growth [25–28]) have been demonstrated to fabricate the paper-based SERS substrates. Expect the separation ability of such substrates, aggregation ability can also be developed to concentrate molecules onto the sharp tip of the paper strip for the ultrasensitive detection. Generally, several orders of the detection skills can be obtained by such concentration ability. Anyway, simplicity, on-site detection, flexibility, portability and cheapness of such paper-based substrates are contributed to its popularity.

However, many holes or vase-like defects are existed on such surface, which are unavoidable and lead to the large losses of incident laser. The overall intensity of the electromagnetic coupling and then the Raman signal of biological molecules are decreased. Obviously, just only one type of the metal nanostructure can not cover all surfaces. Combination of the three-dimensional (3D) AgNFs and AgNPs on the paper substrate is proposed and firstly obtained in our experiment. There are several advantages for the proposed SERS substrates: 1) 3D AgNFs and AgNPs are self-assembled simultaneously; 2) 3D AgNFs, with special fine structure, large specific surface area and large size, are easily guided by the defects (holes and vase-like defects) to avoid the losses of incident laser; 3) Such AgNFs also produce many "hot spots" to enhance the intensity of the EM coupling, which is very important for the SERS sensitivity; 4) The combination of the AgNFs and AgNPs is further enhance

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the EM coupling. The largest enhancement of the EM coupling is obtained by the existence of the AgNFs in the vase-likes defects, which is demonstrated theoretically using commercial COMSOL software; 5) Separation and aggregation abilities are not obviously affected by such combination in our experiment. As a result, as low as 10^{-14} M R6G and CV molecules can be detected without concentration, and the ultralow CV molecules (10^{-21} M) were also detected by preconcentrating them on the tip of the paper card.

2. Materials and methods

2.1. Reagents and materials

Chromatography paper (Whatman 1CHR No. 3001-917), aqueous solution of acidic stannous chloride, AR silver nitrate, ascorbic acid, Rhodamine 6G (R6G), crystal violet (CV), ethanol (99.7%), acetone, were all purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All chemicals were used without further purification.

2.2. Fabrication of the paper sensor

The chromatography paper strip was successively soaked in acidic aqueous solution of $SnCl_2$ (0.2 M) and $AgNO_3$ (0.2 M) for two minutes and then rinsed by pure acetone and water, which was repeated three times to improve the distribution density of silver seeds on the chromatography paper strip. Subsequently, the structures of AgNFs connected with AgNPs arrays were obtained by immersing the paper into the mixed solution of 100 mL $AgNO_3$ (0.1 M) and 50 mL ascorbic acid (0.1 M) for a certain time, followed by air-drying.

2.3. Numerical analysis of electric field distribution

The electric field properties of samples were numerically calculated by commercial COMSOL software. The size, morphology and structure of the samples were extracted by reference to scanning electron microscope (SEM) images. The 532 nm laser was perpendicularly incident on the sample substrates.

2.4. Characterization

Scanning electron microscope (SEM, Zeiss Gemini Ultra-55) detection was employed to elucidate the morphologies of samples. Raman spectra were collected using Horiba HR Evolution 800 excitation with 532 nm Ar excitation laser, laser power of 0.48 mW. The size of laser beam focused on sample was about 1 μm. The SERS spectra on display were the average value of spectra from three different positions.

2.5. Preconcentration process

15 μL CV sample was spotted near the edge of the substrate by capillary tube. A small amount of 99.7% ethanol (3–5 mL) as a mobile phase was poured into a glass beaker which was then covered with a glass lid, which is needed to presaturate the beaker volume with ethanol vapor before the paper substrate with CV droplets was placed into the glass beaker. The paper substrate was then carefully placed upright into the mobile ethanol in glass beaker to concentrate the CV molecules into sharp tip of the substrate. The CV spot on side of paper was in proximity to but did not contact the mobile ethanol meniscus. During the development process, the beaker remained covered to minimize mobile ethanol evaporation from the paper substrates.

3. Results and discussion

A large number of clusters of 3D AgNFs were formed in the holes or "vase" like defects, shown in Fig. 1a–c. The as-synthesized AgNFs were tufted, consisting of a solid core with many long, pin-like, and upstanding nanopillars. These Ag nanopillars started with the Ag seeds deposited in the depression and self-assembled into the tufted nanostructure. These nanopillars showed considerable density on the surfaces of crystals, which indicated the existence of a large amount of "hot spots". Fig. 1d was a simulated electric field distribution image of the defect-guided 3D AgNF in a "vase"-like silverplate, which was designed by Fig. 1b. A high-intensity electric field located throughout the AgNFs surface, indicating the promising performance in the SERS area. In contrast, closed packed AgNPs were obtained on the flat area (shown in Fig. 1b), which were also important for the SERS applications (including our research). Such effects of the AgNPs have been studied by many researchers [21–29]. The details are not studied here.

Basal surface topography and growth processes have big effects on the pattern of Ag nanostructures (AgNSs: AgNFs and AgNPs). Two steps, electroless-deposition Ag seeds and in situ AgNSs growth, were used to create such 3D AgNFs connected with AgNPs arrays on the paper, showed in Fig. 2. Sn^{2+}, deposited by immersing the paper (Whatman grade 1) in an acidic $SnCl_2$ solution (0.02 M), was used to form Ag seed by soaking the paper in aqueous $AgNO_3$ solution (0.02 M) via reduction reaction of $Sn^{2+}(aq) + 2Ag^{+} \rightarrow Sn^{4+}(aq) + 2Ag(s)$. The defects on the paper surface can cause proximity and even adhesion of adjacent bobbins and provide favorable sites for the deposition and aggregation of Ag seeds. Such deposition processes were carried out three times to achieve the denser Ag seeds. And then, in- situ growth was employed to achieve the regrowth of Ag seed through a heterogeneous nucleation and growth mechanism by exposing the paper to mixed solutions consisting of 100 mL of 0.01 M $AgNO_{3,}$ and 50 mL L-ascorbic acid (AA). In this process, as-formed Ag seeds aggregation on the defects began to act as the sites for further irregular AgNFs precipitation after a period of treatment.

Detection sensitivity of such paper-based SERS substrate is studied by using Rhodamine 6G (R6G) and crystal violet (CV) aqueous solutions with varied concentrations as the probe molecules. Fig. 3a and c show the SERS spectra of R6G and CV molecules with various concentrations of 10^{-8}, 10^{-10}, 10^{-12}, 10^{-14} M, respectively. The Raman peaks are in good agreement with previous reports for R6G and CV molecules [30–32]. The characteristic signals of molecules are still visible even as low as 10^{-14}M. Within this concentration range, the SERS intensity show a good linear SERS dependence with the molecules concentration with the high coefficient of determination (R^2) (0.923 and 0.840 respectively for R6G, 0.994 and 0.926 for CV (10^{-6}-10^{-12}M)), shown in Fig. 3b and d. Compared with the enhancement performance of SERS substrates in some previous reports [33,34], the detection sensitivity is further improved by the paper-based silver nanoflowers (AgNFs)/silver nanoparticles (AgNPs) array hybrid substrates. The excellent Raman enhancement performance may be attributed to the following two aspects. First, the utilization of paper substrates with hydrophilic property improves the density of distribution of enhancement media and adhesiveness target organic molecule; second, combination of the three-dimensional (3D) AgNFs and AgNPs on the paper substrate avoid the losses of incident laser and further enhance the intensity of EM coupling.

Besides the high-sensitivity enhancement performance, reproducibility of the SERS-based substrates is another critical factor for SERS substrates in the practical application. Still, the reproducibility performance of as-grown paper-based SERS substrates was investigated using both R6G and CV as the probe molecules. SERS spectra of R6G molecules were collected from different spots on