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Investigation of 3D silvernanodendrite@glass as surface-enhanced Raman scattering substrate for the detection of Sildenafil and GSH

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HIGHLIGHTS

- A new three-dimensional (3D) silvernanodendrite@glass film was synthesized.
- The influence of ions on the Raman activity of this film was analyzed.
- The superiority of the film in practical application of SERS was verified.
- The absorption mechanism of **GSH** on the film through the peptide bond was analyzed.

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ABSTRACT

A solid-phase dendritic Ag nanostructure was synthesized in the presence of silk fibroin biomacromolecule and planted on the glass to form three-dimensional (3D) silvernanodendrite@glass film. When NO_3^-, Cl^- and SO_4^{2-} were added in the synthesis process of the film to study their influence on the Raman activity of this substrate using MB as probe molecule, it's found that the substrate with Cl^{-1} gives the most intensive enhancement, and two ways were proposed to explain this phenomenon. Its superiority in practical application of surface-enhanced Raman scattering (SERS) was verified by analyzing the characteristic Raman spectrum of Sildenafil between 1150 cm^{-1} and 1699 cm^{-1}. Besides, the absorption mechanism of **GSH** on the film through the role of peptide bond was analyzed. **GSH** interacts strongly with the silver surface via the ν(C—S) in two different conformers. The carboxyl and the amide groups are also involved in the adsorption process. In this experiment, we synthesized, studied and applied this as-growth substrate and found some information about its interaction with different molecular bonds and functional groups of peptide.

1. Introduction

Morphology-controlled synthesis of noble metal with uniform sizes and structures has been rapidly developed into a promising field not only for their intrinsic chemical and physical properties, but also for SERS and catalytic properties of functional materials [1–4]. In particular, Ag nanostructures, have gained great research interest for the important applications in catalysis [5] and SERS as excellent substrates [6,7]. To date, a series of modified Ag nanostructures with different structural features and special uses have been successfully prepared by different strategies including templated and templatless synthesis, for example: spheres and tetrahedral quantum dots [8–12]; nanowires, nanorods and nanobelts (1D) [13–15]; nanoplates and triangular plates (2D) [16–20]; nanocages and branched multipods (3D) [21–23].

Silk fibroin (SF) biomacromolecule has been found to be a good biological framework as forming branched nanostructures for its unique characteristic [24,25]. The fabrication of nanoparticles adsorbed on this new material to form dendritic nanostructure has promising applications in surface-enhanced materials [26,23,27]. In the past 2 years, a mild, wet-chemical method had been taken out to fabricate dendritic Ag nanostructure (DAN) based on solution-phase procedures [28–30]. However, some problems about the concentration and uneven distribution of the DAN are still alive in this colloid. Now, this nanostructure is tried to plant on glass surface through 3-aminopropyltriethoxy silane (APES). Compared with the monodispersed DAN colloidal solution, its growth pattern will be more stable and can be kept for a long time without precipitation. Furthermore, this hierarchical silver nanodendrite has a much more rough surface and greater Raman scattering cross section. A possible formation mechanism of the film is proposed based on previous studies and its Raman enhancement mechanism is further analyzed by studying the influence of ions on the Raman activity of this substrate using MB as probe molecule.

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Recently, there are more illegal additives in the field of Chinese health medicine, in order to identify these counterfeit drugs, we propose a SERS method based on this substrate for the trace detection of Sildenafil, which is the principal component of Viagra® tablets. Besides, there is few reports on the interaction between DAN and protein, so the SERS of GSH (short peptide) is investigated and the vibrational modes of the representative functional groups are analyzed. GSH is an antidote and antioxidant which contains an unusual peptide linkage between the amino group of cysteine and the carboxyl group of Glutamate side chain. The thiol group, as an active group of GSH, is kept in a reduced state. This paper investigates the structural characteristic and usability of this new substrate in SERS and analyzes the adsorption mode of short peptide on this film. It will provide a potential method to analyze and identify moleculars and polypeptides in the future [31].

2. Experiment

2.1. Instrumentation

The scanning electron microscopy (SEM) images of dendritic Ag nanostructure was obtained with a scanning electron microscope system operating at 30 kV. The XRD analysis was performed using D/MAX2200VPC (40 kV/40 mA). SERS spectra were obtained with a 1200 gr/mm holographic grating spectrometer (Acton Spectro@2300i, Princeton Acton, USA). The spectral resolution was set at 4 cm^{-1}. An air cooled CCD detector (Pixis 256, Princeton Acton, USA) was used for measuring the Raman signal by an integration method. The 514.5 nm line of an argon ion laser was used as the excitation source for Raman and SERS measurements. The laser power at the samples was 10 mW. The absorption spectra were detected by spectrophotometer (Lamda 35, PE company, USA). The data processing was operated using Origin 7.5 software.

2.2. The synthesis of dendritic supramolecular Ag nanostructures

For a typical synthesis of DAN, the SF aqueous solution was prepared according to the previous method [32] to a final concentration of approximately 15 wt.%. 100 mL $AgNO_3$ aqueous solution (0.05 M) was added to 0.2 g of prepared SF solution at room temperature for 6 h without stirring, and then the dendritic supramolecular Ag nanostructures could be obtained.

2.3. "Plant trees" on the silane-treated surface of the glass

First, clean the glasses in acetone, ethanol and distilled water using ultrasonic for 10 min respectively to remove the grease and other impurities on the surface. Then clean them in the Piraha solution [H_2SO_4: 30% H_2O_2 = 7: 3 (V/V)] for 1 h. After being taken out, they were repeatedly washed with distilled water and dried by N_2.

Put the glasses into 0.1 wt.% of APES solution for 2 h, after washed and dried as before, then get them into dendritic Ag nanostructure sol (DANS) respectively for 2 h, 4 h, 8 h and 12 h, followed by solvent evaporation in air. Then the 3D silvernanodendrite@glass film was prepared.

2.4. Collect the samples' Raman signal

The SERS spectrum of MB, Sildenafil, and **GSH** was collected in this paper. Firstly, A group of silvernanodendrite@glass films were formed in the DANS with NO_3^-, Cl^-, SO_4^{2-}, the SERS signal of MB was collected with the same concentration by dropping a 1 mL of sample separately onto films. Secondly, another group of glasses were immersed in DANS with different time to form films, then the SERS of Sildenafil with the same concentration (10 mg/L) was tested on them. For comparison, it was also directly measured in the DANS (with different proportions) and sodium borohydride-reduced silver colloid. Its normal Raman spectrum was also collected to get the standard peaks of this drug. At last, the **GSH** solution with different concentration was prepared, then the group of glass films were put into the solution to absorb GSH molecules for 30 min. After being taken out, they were repeatedly washed with ethanol to remove residual GSH molecules. The absorption and Raman spectrum were obtained at room temperature.

3. Results and discussion

3.1. The formation process of 3D sliver nanodendrite film

The morphology and nanostructure of the Ag nanosturcture has been studied by Xia [33] using transmission electron microscopy (TEM), scanning electron microscopy (SEM) and selected area electron diffraction (SAED) from the prepared solution, which shows that both the shape and size of as-synthesized Ag nanostructures are dependent on the reaction duration. Through the dual role of tyrosine (Tyr), ions are firstly reduced to silver nanoparticles as 'leaves' of the nanodendrite and then these 'leaves' are attached on the SF biomacromolecules to finally form the branches. In this whole process, silver particles are gradually aggregated to form DAN (Fig. 2a–d) under the driving force of diffusion limited aggregation (DLA) [34,35], which is usually used for explaining the phenomena in non-equilibrium reactions. The XRD pattern recorded from the DAN is displayed in Fig. 2i. The peaks are assigned to direction from the (111), (200) and (220) of face-centered cubic (fcc) Ag (JCPDS, 04-0784) [36].

In the subsequent process, these branched nanostructures are adsorbed on silane-treated surface of glass as growing points through the adsorption template of alkyl chain. SF biomacromolecules continue to play a capping agent role to lower the surface energy of silver [111] facets through the direct interaction with the silver surface [33]. Based on previous microstructure analysis, silver particles adhere to the same crystal surface to form single crystalline structure with a certain extent of preferential crystal orientation, resulting in a slow growth on the silver nuclei of branch along the [111] orientation (in which stem probably grows along [110] direction and two leaves grow along [011] and [101] directions, respectively) [37]. Finally, the dendritic nanostructures in the solution disappear and nanoclusters grow to the certain size (ca. 10 ± 5 μm) on the glass. The whole process is illustrated diagrammatically in Fig. 1. Fig. 2e–h shows the SEM images of this dendritic silver structure grows to several remarkable hierarchical generations in different stages of the synthesis, confirming the dendrite-like morphology. UV–vis absorption spectrum shows the dynamic change of structure scale. The spectrum band at ca. 425 nm undergoes a red shift (plasmon absorbance of silver particles λ_{max} = 400 nm) with the increase of the size of DAN. The double-peaked character can be explained by the sphere-cluster model [38]. In summary, the formation of the DAN is dominated by both diffusion and oriented attachment [39].

3.2. The SERS of MB on 3D silvernanodendrite@glass film prepared with NO_3^-, Cl^- and SO_4^{2-}

To study the activity of this substrate and its interaction with the ions, the UV–vis absorption spectrum of the substrate and SERS spectrum of MB is collected. as is shown in Figs. 3 and 4.

Compared with the corresponding spectrum of MB obtained without aggregating agent (Fig. 4d), it's observed that the relative intensity of the spectrum are significantly affected by anions added in the film. The intensity ratio (I_a/I_d, I_b/I_d and I_c/I_d) of some strong