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A reagent-assisted method in SERS detection of methyl salicylate

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ABSTRACT

With the explosive application of methyl salicylate (MS) molecules in food and cosmetics, the further detection of MS molecules becomes particularly important. Here we investigated the detection of MS molecules based on surface-enhanced Raman scattering (SERS) in a novel molecule/assistant/metal system constructed with MS, 4,4′-(hexafluoroisopropylidene) bis (benzoic acid) and Ag nanoparticles (AgNPs). The minimum detection concentration is 10^{-4} M. To explore the function of assisted reagent, we also referred another system without assistant molecules. The result demonstrates that SERS signals were not acquired, which proves that the assistant molecules are critical for the capture of MS molecules. Two possible mechanisms of MS/assistant/AgNPs system were speculated through two patterns of hydrogen bonds. The linker molecules acted as the role of the bridge between metallic substrates and target molecules through the molecular recognition. This strategy is very beneficial to the expanding of MS detection techniques and other hydrogen bond based coupling detections with SERS.

1. Introduction

More and more people pay attention to salicylic acid (SA) and its ramification because they are closely linked with us in pesticide, medicine, cosmetics and foods [1]. SA is an essential material in the preparation of many chemical products [2], such as antiinflammatory [3] and antipyretic agent [4]. And SA is mainly consumed in human medicine as an analgesic [5] and antipyretic drug [6], being active in preventing platelet aggregation [7].

As a typical ramification of SA, methyl salicylate (MS) is an important ester compound and has been widely used as solvents, preservatives and cosmetics in the spices [8] and pharmaceuticals [9]. On one hand, MS can promote blood circulation, improve the nutritional supply and reduce the local pathological response [10,11]. On the other hand, MS has also antipyretic, analgesic and anti-rheumatic effects [7]. It is so important that it is very meaningful to understand the relationship about structure and function via accurate detection.

There are many methods for detecting MS molecules, such as fluorescence analysis [12], gas chromatography [4], and so on. Among them, the most usually used method is the mass spectroscopy. The advantage of mass spectrometry is its high sensitivity, which can reach to ppm even ppb detections. Mass spectrometry also has the advantage of reliability and versatility, which can measure almost all of the materials' compositions and structures. However, the disadvantage of mass spectrometry is that it normally needs expensive instruments, professional staff and complex pre-processing process. Thus the development of simple and convenient methods is still necessary and worthy of study.

The surface-enhanced Raman scattering (SERS) technique obtained more and more attention since it was discovered on a rough silver electrode in 1974 [13,14]. Because of its high sensitivity, high selectivity, and nondestructive trace detection [15], it has been widely applied to many fields, such as chemical analysis, environmental monitoring, biological assays and medical diagnosis [16–19]. SERS is a powerful tool for the study of structure, property and orientation of molecules adsorbed on metal surfaces [9]. It also shows great potential in combining new techniques in strict detection requirements. In this paper, SERS was employed as a main strategy to detect MS molecules. A novel intermolecular connection technique was designed to assist the SERS detection of MS molecules.

In general the direct SERS detection of MS molecules faces the difficulty of neither adsorption of MS on solid SERS substrates nor soluble in SERS colloid solutions. So it is very necessary to find a way to trap the MS molecules dwelling on the SERS substrates. In the present study, an assistant molecule of 4, 4′-(hexafluoroisopropylidene) bis (benzoic acid) was used to fulfill the planning strategy. Because the assistant molecule can generate intermolecular hydrogen bonds with MS, the targeting molecules of MS are then captured on the SERS substrates through a molecule/assistant/metal structure. In this system, the

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assistant molecule has the bridging effect between silver nanoparticles and target molecules. The employment of the linker molecule base on hydrogen bonds is one aspect of the innovation. Further, the introduction of the strongly electron-withdrawing groups of —CF_3 in linker molecules is another important innovation. The —CF_3 groups have a great contribution to the formation of hydrogen bonds in the system, leading to the delocalization of electrons and changes of molecular polarizability [20], also resulting in an enhanced spectral output. In this process signals of MS molecules are enhanced for improved detections.

In addition, unlike other detecting methods which generally require complicated pretreatment processes to obtain suitable solution samples [21], our SERS detection of MS molecules can be performed directly in original solutions, which shows a potential simple and feasible detection of MS in real world. However, before the final real-world detecting application, the incipient research is focusing on the mechanism, especially on the intermolecular structure, which is the basis of this new method. This novel detection method not only expands the application of SERS for the detection of MS but also provides a proof-of-concept to construct hydrogen bond connection between the SERS substrates and targeting molecules through the provided linker molecules. This method also shows the potential of applications of SERS in other hydrogen bond based coupling detection systems.

2. Experimental

2.1. Chemicals

$AgNO_3$ (99%) were obtained from Wako Pure Chemical Industries, Ltd. Methyl salicylate and 4,4′-(Hexafluoroisopropylidene) bis (benzoic acid) was purchased from Sigma-Aldrich Inc. Trisodium citrate (98%) was purchased from Shanghai Chemical Reagent Co., Ltd. Ethyl alcohol was obtained from the Beijing Chemical Reagent Plant. All chemicals were analytic grade and were used without further purification. Deionized water (18.6 $\Omega \cdot cm^{-1}$) was obtained with a Milli-Q system (Millipore).

2.2. Preparation of AgNPs

AgNPs with an average diameter of 52 nm were prepared according to our previous work [22–24]. In a typical synthesis, 36 mg of $AgNO_3$ was dissolved in 200 mL of water in a flask. This aqueous solution was then heated to boil under stirring and reflux. A total of 4 mL of trisodium citrate solution (1:1, w/v) was added into the flask and allowed to react for 1 h.

2.3. Fabrication of MS/Assistant/AgNPs Self-assembly

Firstly, 5 mL Ag sol was concentrated to 1 mL through 5000 rpm for 5 min. Secondly, 25 μL ethanol solution of the assistant molecule was added into the 1 mL concentrated Ag sol under ultrasound. Thirdly, the liquid MS was added under ultrasound. Fourthly, 4 mL deionized water was added under ultrasound. Thus a solution containing MS/assistant/AgNPs self-assembly was obtained. The final volume of the solution is 5 mL. According to experimental needs, the final concentration of the assistant molecule was tuned to be 10^{-3}, 10^{-4}, and 10^{-5} M, respectively. The final concentration of MS was controlled to be 10^{-1}, 10^{-2}, 10^{-3}, and 10^{-4} M, respectively.

2.4. Characterization

Raman spectra were recorded on a LabRam Aramis Raman Microscope system (Horiba–Jobin Yvon), excited by 532 nm line (Melles Griot). The typical acquisition time was 10 s. The solution was loaded in glass capillary tubes for the spectral acquire. The morphologies of the substrate were examined by a Hitachi H-800 transmission electron microscope (TEM).

3. Results and Discussion

Fig. 1 shows the fabrication processes of MS/assistant/AgNPs system. First, a 25 μL ethanol solution of the assistant molecule was dissolved in 1 mL concentrated Ag sol with stirring. The color of the Ag sol changed a little lighter after a sufficient mixing. The assisted molecules were chemically absorbed the surface of AgNPs through the Ag—OOC bonds. Subsequently, MS molecules were added into the resultant solution. MS was dispersed quickly after shaking the solution. The MS were dissolved and no color change was observed. We believe a complex assembly nanostructure of a MS/assistant/AgNPs system was established. In the comparative experiment all the procedure were repeated except without the assistant molecules. In this control experiment, the MS cannot be dissolved in the colloid solution. Thus the linker molecules must play an important role on assisting the coupling between the MS and AgNPs. We speculated that two different patterns of hydrogen bonds could be formed in the complex nano-assemblies. According to the structures and functional groups of the linker molecules and MS, each of them has an electron-withdrawing group and an electron-donating group. By the combination of the pair of electron-withdrawing groups and electron-donating groups, two different combination ways can be formed. One is the coupling of the carbonyl of MS and the hydroxyl of the linker molecules [9]. The other is the coupling of the hydroxyl of MS and the fluorine of the linker molecules. These two hydrogen bonds are illustrated in the Fig. 1. The richness of the intermolecular hydrogen bonds solves a significant problem on the non-adsorption of the MS on SERS substrates, which is the major obstacle for the detection of MS by SERS.

Fig. 2 shows the TEM image of the AgNPs. The AgNPs are monodispersed in size. The size distribution was counted using a Lorentz distribution. The main range is from 35 to 65 nm as shown in the inset of Fig. 2. The percentage of 35, 40, 45, 50, 55, 60 and 65 nm is 2.5%, 3.5%, 21%, 27.5%, 23.5%, 16.5% and 5.5%, respectively. The average size is 52 nm. The mono-dispersion of the NPs is advantageous to obtain reproducible SERS signals when the NPs are used as SERS substrates. The morphology of AgNPs is approximately spherical. The symmetrical characteristic of these NPs guaranteed the uniform adsorption patterns of molecules on surfaces and uniform spectral gains.

Fig. 3A shows the Raman/SERS spectra of liquid MS, the linker molecule of 4,4′-(hexafluoroisopropylidene) bis (benzoic acid) powder, and the assembly complex of the MS/linker-molecule/AgNPs. The concentration of both 4,4′-(hexafluoroisopropylidene) bis (benzoic acid) and MS for self-assembly of the complex is 10^{-3} M. The Raman bands of MS molecules located at 563, 667, 810, 1034, 1252, 1441, 1466, 1615, and 1676 cm^{-1} are assigned to the out-of-plane of benzene

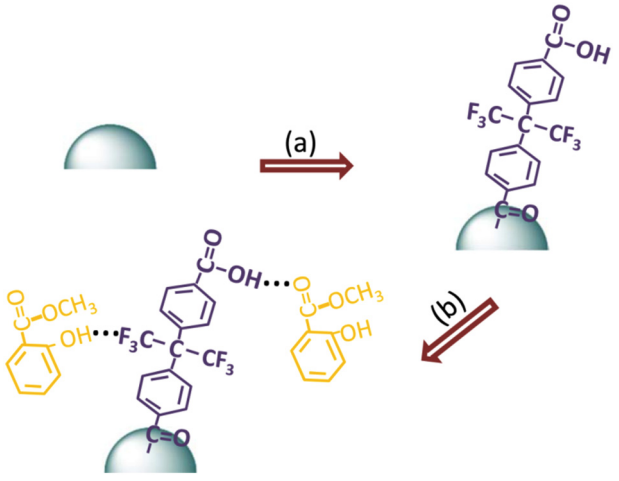

Fig. 1. The schematic of the fabrication process of linker molecule assisted assembly complex for the SERS detections.