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Quantitative SERS analysis based on multiple-internal-standard embedded core-shell nanoparticles and spectral shape deformation quantitative theory

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ABSTRACT

Due to the practical impossibility in controlling the number and distribution of "hot spots" on or close to the surfaces of enhancing substrates, internal standards are generally used to improve the accuracy and precision of quantitative surface-enhanced Raman spectroscopy (SERS). Traditional internal standard methods based on either univariate ratiometric models or conventional multivariate calibration models can use the information of only one characteristic SERS peak of only one internal standard, which weakens the efficiency of traditional internal standard methods in improving the quantitative results of SERS assays. In this contribution, the concept of using multiple internal standards was introduced for the first time to quantitative SERS assays by incorporating a unique spectral shape deformation (SSD) quantitative theory with multiple-internal-standard embedded core-shell nanoparticles. The quantification of phosmet residues on apple skins by SERS technique with Au-core/Ag-shell nanoparticles embedded with both 2-MB and PATP as enhancing substrate was used to illustrate the applicability of the proposed strategy. Experimental results demonstrated that the proposed multiple-internal-standard strategy based on SSD achieved much more accurate and precise concentration predictions for phosmet residues on apple skin than traditional single-internal-standard methods based on either univariate ratiometric calibration models or conventional multivariate calibration models. The SERS quantitative results of the multiple-internal-standard strategy were comparable to those obtained by LC-MS/MS. The average relative deviation between the quantitative results of the proposed method and those of ICP-MS was about 8%. The good accuracy of the proposed method makes it a promising alternative for quantitative SERS assays.

1. Introduction

Surface-enhanced Raman spectroscopy (SERS) has features of high sensitivity, excellent molecular specificity, and simple sample pretreatment, and has been considered to be an ultrasensitive detection method for a variety of applications [1,2]. However, SERS is still recognized as a qualitative technique rather than a quantitative one. The main reason hindering the application of SERS technique to quantitative assays is that the enhancement of SERS signals largely depends on the enhancing substrates. Besides the classic noble metal (predominantly Au or Ag) nanoparticles, various fancy SERS-activate substrates, such as silver nanoshells [3], Au nanoparticles grafted on dendritic α-Fe_2O_3 [4], gold nanorods [5], silver-coated gold bimetallic nanoparticles [6], etc have been fabricated and applied to SERS assays. Even though these enhancing substrates possess all sorts of advantages, none of them can ensure good quantitative results in SERS assays due to the practical impossibility in controlling the number and distribution of "hot spots" (highly enhanced electromagnetic fields) on or close to the surfaces of enhancing substrates.

In order to improve the accuracy and precision of quantitative SERS assays, internal standard methods have been used to correct SERS intensity variations induced by the variations in physical properties of enhancing substrates [7,8]. Internal standard methods adopted in quantitative SERS assays can be roughly classified into three categories (Fig. 1), i.e. internal standard addition detection mode [9,10], internal standard tagging detection mode [7,11,12], and generalized ratiometric SERS indicator based detection mode [13]. Both internal standard addition detection mode and internal standard tagging detection mode may encounter the problem of dynamic exchange or competitive adsorption between the internal standards and the target analytes. Generalized ratiometric SERS indicator based detection mode involves tagging a SERS probe onto the surface of enhancing substrates which can

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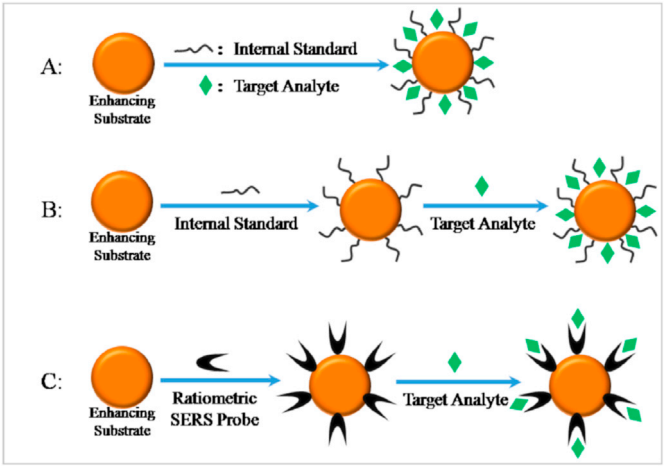

Fig. 1. Quantitative SERS detection modes: A) internal standard addition detection mode, B) internal standard tagging detection mode, and C) generalized ratiometric SERS indicator based detection mode.

react with the target analyte to induce deformations of its SERS spectrum. The target analyte itself cannot be adsorbed onto the surface of SERS enhancing substrates. There is no problem of competitive adsorption between the SERS probe and the target analyte. Accurate quantitative information of the target analyte can be extracted from the deformed SERS spectrum of the SERS probe by an advanced quantitative analysis model based on spectral shape deformation [14]. But it is not easy to find or synthesize a proper SERS probe for a specified analyte. As a result, compared with the other two detection modes, the application of generalized ratiometric SERS indicator based detection mode is relatively limited.

There have been some attempts to solve the problem of competitive adsorption between internal standards and the target analytes by using internal standards embedded core-shell nanoparticles as enhancing substrates [15,16]. Moreover, the internal standards embedded inside core-shell structures will not be influenced by the microenvironment around the enhancing substrates and hence avoid possible dynamic dissociation. Even though SERS assays by the use of internal standards embedded core-shell nanoparticles as enhancing substrates offer some advantages over conventional SERS assays based on either internal standard addition detection mode or internal standard tagging detection mode, they still generally adopt the same univariate ratiometric model based on peak area/height ratios between the characteristic SERS peaks of the target analytes and the internal standards for quantitative assays. A prerequisite for the application of univariate ratiometric models based on peak area/height ratios is that the internal standard must have one or more SERS peaks in spectrally silent regions of the target analytes, other coexisting SERS-active compounds and possible background interference(s). Such a requirement poses some difficulty in selecting an appropriate internal standard for quantitative analysis of a specific analyte of interest. Recently, a unique spectral shape deformation (SSD) quantitative theory based on multiplicative effects model [11,14] has been proposed and successfully applied to quantitative spectroscopic analysis of complex systems including quantitative SERS assays. SSD not only relieves the requirement of distinctive SERS peaks on internal standards used in quantitative SERS assay, but also frees the analysts from suffering from the peak selection dilemma. During the quantitative SERS analysis of a specific analyte of interest, SSD takes the advantage of the whole SERS spectrum rather than one characteristic SERS peak of an internal standard to correct SERS intensity variations induced by the variations in physical properties of enhancing substrates. Moreover, SSD allows the use of multiple internal standards to quantify the analyte of interest. The multiple-internal-standard method based on SSD was applied to quantitative LC-MS/MS and achieved better quantitative results than tradition single-internal-standard method especially when one has no much clue on which chemical compound should be selected as internal standard from several possible candidates [17]. Inspired by its success in LC-MS/MS, in this contribution, the multiple-internal-standard method based on SSD was tentatively integrated with Au-core/Ag-shell nanoparticles with a view to improving the accuracy and precision of quantitative SERS assays. The core-shell nanoparticles with embedded multiple internal standards were applied to the quantitative SERS analysis of phosmet (phosphorodithioic acid S-[(1,3-dihydro-1,3-dioxo-2-H-isoindol-2-yl) methyl] O,O-dimethyl ester) residues on apple skin, and its performance was compared with core-shell nanoparticles with embedded single internal standard.

2. Experimental

2.1. Reagents and chemicals

Silver nitrate ($AgNO_3$), ascorbic acid and potassium chloride were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Trisodium citrate dihydrate ($C_6H_5Na_3O_7{\cdot}2H_2O$) and Zonyl FSN-100 were bought from Sigma-Aldrich Chemical Reagent Co., Ltd. (Shanghai, China). Concentrated HCl (guaranteed reagent) and HNO_3 (guaranteed reagent) were provided by Zhuzhou Research Institute of Chemical Industry (Zhuzhou, China). 2-Mercaptobenzimidazole (2-MB, 98%) and ethanol were supplied by Titanchem Co., Ltd. (Shanghai, China). Chlorauric acid hydrated ($HAuCl_4{\cdot}4H_2O$), phosmet (HPLC grade) and p-Aminothiophenol (PATP, 97%) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), J&K Scientific Ltd. (Beijing, China) and Adama Reagent Co., Ltd (Shanghai, China), respectively. Methanol (HPLC grade) and acetonitrile (HPLC grade) were purchased from Oceanpak Alexative Chemical Co., Ltd. (Beijing, China). Apples were bought from a local supermarket in Changsha, China. The chemicals with their degree of purity not being specifically stated were of analytical grade. All chemicals were used as received without any further purification. Ultrapure water (18.2 MΩ cm) produced by an Aquapro water system (Chongqing, China) was used throughout the experiments.

2.2. Synthesis of Au nanoparticles (AuNPs)

All glassware were soaked in fresh aqua regia ($HCl:HNO_3 = 3:1$ V/V) overnight, and rinsed six times with ultrapure water. AuNPs of about 40 nm diameter were synthesized according to the sodium citrate reduction method [18]. Briefly, 100 mL of aqueous solution of $HAuCl_4$ (0.01%, m/V) was heated to boil under frequent stirring. Then 1 mL of sodium citrate solution (1.25%, m/V) was rapidly added into the boiling solution of $HAuCl_4$. Subsequently, the mixture was heated for 30 min to ensure complete reduction, and then cooled to room temperature. The resulting AuNPs solution was stored in a dark bottle at 4 °C for later use.

2.3. Preparation of core-shell nanoparticles with embedded internal standards

Core-shell nanoparticles with embedded internal standards, Au@2-MB@Ag, Au@PATP@Ag and Au@2-MB + PATP@Ag were prepared by a modified method based on the procedure reported in literature [15,16]. The experimental procedures were depicted in Fig. 2 and briefly described as follows. 8 mL of AuNPs solution was centrifuged at 9000 rpm for 15 min. The obtained precipitates were re-dispersed in 4 mL ultrapure water. 200 μL of FSN (0.5%, m/V) was added into the solution under constant stirring to stabilize AuNPs. Subsequently, the surfaces of AuNPs were modified by different internal standards through the addition of 10 μL 2-MB (50 μM), 10 μL PATP (50 μM), or mixture of 10 μL 2-MB (50 μM) and 10 μL PATP (50 μM), respectively. After 6 h of continuous stirring, the mixture was centrifuged twice at 9000 rpm for 15 min to remove excessive 2-MB, PATP, or both 2-MB and PATP. The obtained precipitates were re-dispersed in 4 mL ultrapure water. And

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