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Surface enhanced infrared absorption spectroscopy based on gold nanostars and spherical nanoparticles

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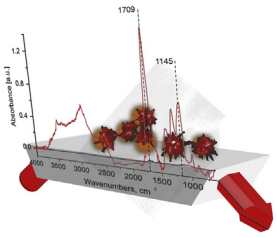
HIGHLIGHTS

- Signal enhancement from two analytes at plasmonic nanostars and nanospheres were compared for SEIRAS in IR-ATR.
- The signal obtained from nanostars was at least 2-times higher in comparison with nanospheres.
- Up to 10-times signal enhancement at plasmonic nanostars for SEIRAS was observed.
- Dependence of enhancement on the number of nanostars at the internal reflection element surface was demonstrated.
- SEIRA signal was correlated to the concentration of analyte molecules present within the evanescent field.

GRAPHICAL ABSTRACT



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ABSTRACT

Plasmonic anisotropic nanoparticles possess a number of hot spots on their surface due to the presence of sharp edges, tips or vertices, leading to a high electric field strength surrounding the nanostructures. In this paper, we explore different plasmonic nanostructures, including anisotropic gold nanostars (AuNSts) and spherical gold nanoparticles, in surface-enhanced infrared absorption spectroscopy (SEIRAS) in an attenuated total reflection (ATR) configuration. In our experiments, we observed up to 10-times enhancement of the infrared (IR) absorption of thioglycolic acid (TGA) and up to 2-times

Abbreviations: ATR, attenuated total reflection; AuNSts, gold nanostars; BSA, bovine serum albumin; c-NPs, citrate-capped spherical nanoparticles; CTAB, cetyltrimethylammonium bromide; EF, enhancement factor; RSD, relative standard deviation; IR, infrared; IRE, internal reflection element; MCT, mercury–cadmium–telluride; La-NPs, laser-ablative gold nanoparticles; LOD, limit of detection; LOQ, limit of quantification; PH, plasmon hybridization; SAMs, self-assembled monolayers; SEIRAS, surface-enhanced infrared absorption spectroscopy; SEM, scanning electron microscopy; SERS, surface enhanced Raman scattering; Si, silicon; TEM, transmission electron microscopy; TGA, thioglycolic acid.

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enhancement of signals for bovine serum albumin (BSA) protein on plasmonic nanostructure-based films deposited on a silicon (Si) internal reflection element (IRE) compared to bare Si IRE. The dependence of the observed enhancement on the amount of AuNSts present at the surface of the IRE has been demonstrated. Quantitative studies with both, TGA and BSA were performed, observing that the SEIRA signal can be correlated to the concentration of analyte molecules present within the evanescent field. The calibration curves in the presence of the AuNSts showed enhanced sensitivity as compared with the bare Si IRE. We finally compare efficiencies of anisotropic AuNSts and spherical citrate-capped and "bare" laser-synthesized gold nanoparticles as SEIRAS substrates for the detection of TGA and BSA. The signal obtained from AuNSts was at least 2 times higher for TGA molecules in comparison with spherical gold nanoparticles, which was explained by a more efficient generation of hot spots on anisotropic surface due to the presence of sharp edges, tips or vertices, leading to a high electric field strength surrounding the AuNSts.

1. Introduction

The enhanced electromagnetic field strength of gold nanoparticles (AuNPs) due to plasmon excitation [1] may be exploited for surface-enhanced vibrational spectroscopies such as surface-enhanced infrared absorption spectroscopy (SEIRAS) [2]. SEIRAS is capable of providing molecular information on analyte molecules located in close vicinity to metallic islands or nanostructures. Furthermore, material-specific vibrational absorptions in the IR-fingerprint region enable unambiguous molecular identification [3]. SEIRA in an attenuated total reflection (ATR) configuration was first reported by Hartstein et al. [2]. ATR spectroscopy takes advantage of total internal reflections within an internal reflection element (IRE) or waveguide [4,5]. SEIRAS in an ATR configuration was previously used to investigate chemical interactions between SEIRA-active layers and various chemicals [6], for the analysis of biological species [7], to monitor the adsorption kinetics of bovine hemoglobin on AuNP films with an improved detection sensitivity (i.e., up to 3 orders of magnitude) [8] and to study the adsorption behavior of cytochrome C at carboxylic acid and hydroxyl terminated self-assembled monolayers immobilized at gold surfaces [9]. In addition, López-Lorente et al. in situ monitored the synthesis of bare AuNPs mediated by stainless steel as reducing agent via SEIRA-ATR spectroscopy [10,11].

Typically, as a first step in SEIRAS studies AuNPs [8,12,13] are periodically structured at the crystal surface providing for two-dimensional arrays. Deposition techniques include sputtering [14], lithography [15] and vapor phase or wet chemical deposition [16]. In a second step, analyte molecules are administered at the arrayed gold surface. In the present study, gold nanostructures were interacted and assembled with analyte molecules in colloidal solution prior to the formation of AuNP arrays at Si ATR waveguide surfaces by adapting a procedure from Seelenbinder et al. [17].

Notably, the signal enhancement strongly depends on the sharpness of AuNP edges, tips or vertices, which are directly related to the intensity of the electromagnetic field surrounding AuNPs [18]. From that point of view, anisotropic AuNPs such as nanorods [19], nanoshells [20], or nanocages [21] are potential amplifiers. However, these types of AuNPs have several limitations including elaborate and time-consuming synthesis. In contrast, AuNSts synthesized via seed-mediated methods [22] require a minimum of neat compounds in a straightforward procedure, and appear to be excellent electromagnetic field enhancers owing to the large number of hot spots at the surface associated with the sharp tips. Moreover, according to the plasmon hybridization (PH) model [23] the core-tip structure serves as an antenna increasing both, the excitation cross section and the electric field enhancement of nanostar plasmon modes [24]. To the best of our knowledge, only a few research groups have applied IR-ATR spectroscopy for monitoring the growth kinetics of such particles [25] and have analyzed the surface chemistry of the AuNSts in details [26]. Last but not least, AuNSts have not been applied in ATR-SEIRAS to date.

In this work, different gold nanostructures (nanostars, ligand-protected or bare spherical nanoparticles) have been deposited together with analytes on a Si IRE and their responses in ATR SEIRAS compared. In our tests, so prepared SEIRAS substrates were used to study the signal enhancement of bovine serum albumin protein (BSA) and thioglycolic acid (TGA). TGA, which was previously investigated in various analytical studies [27,28], was selected as an exemplar of small molecule. BSA, was selected as an extensively studied example of a large molecule within the family of serum albumins, and is among the most important blood carrier proteins [29]. The present study demonstrates that for both TGA and BSA examples an enhancement of the IR-signal due to the presence of the AuNPs was achieved, as compared to IR-ATR results obtained at the bare Si surfaces. This enhancement directly related to the amount of Au nanostructures present within the evanescent field. SEIRA signals obtained with AuNSts have also been compared to results obtained at alternative gold nanostructures with a spherical shape using both, citrate-capped and bare Au nanospheres. The presented results demonstrate that the signal enhancement produced by AuNSts is elevated in comparison to spherical AuNPs, which is explained by a much larger electromagnetic field strength at sharp tips on their surface. These data demonstrate a high potential of gold nanostars in surface-enhanced infrared absorption spectroscopy.

2. Materials and methods

2.1. Chemicals

Gold (III) chloride trihydrate ($HAuCl_4 \times 3H_2O$), trisodium citrate dihydrate ($C_6H_5O_7Na_3 \times 2H_2O$), hydrochloric acid (HCl), L(+)-ascorbic acid (AA), silver nitrate ($AgNO_3$), thioglycolic acid (TGA), bovine serum albumin (BSA) were purchased from Sigma-Aldrich (St. Louis, USA) at the highest purity grade available. Milli-Q water (resistivity 18.2 MΩ cm at 25 °C; Millipore, USA) was used in all preparations. Prior to synthesis, the glassware was washed with a mixture of nitric acid and hydrochloric acid (HNO_3/HCl 1:3 mixture, aqua regia).

2.2. Synthesis of gold nanostars

AuNSts were fabricated by a modified seed-mediated growth protocol by Yuan et al. [29] with minor modifications [30]. Seeds were prepared using the citrate reduction method introduced by