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SERS-active sorbent based on aluminum oxide loaded with silver nanoparticles

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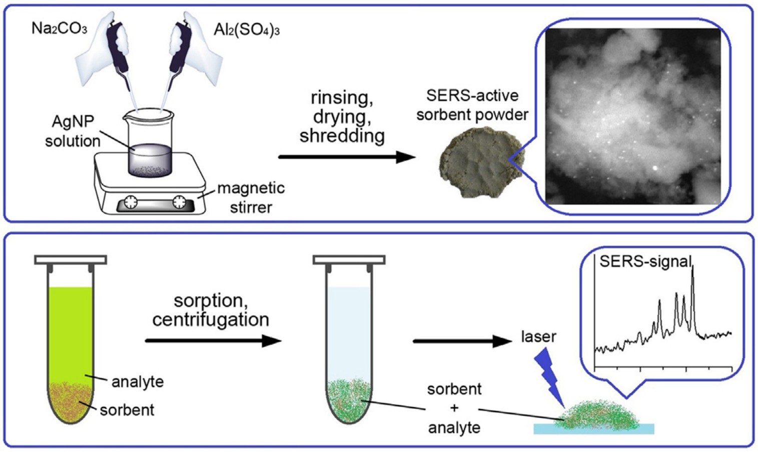
HIGHLIGHTS

- Application of alumina loaded with AgNP as novel SERS-active sorbent for SPE is proposed.
- New synthesis of the sorbents based on alumina loaded with silver nanoparticles is described.
- Sorption properties of these sorbents are investigated with rhodamine 6G and folic acid.
- Results of artificial aggregation of AgNP on SERS enhancement of the sorbents are shown.
- Results of SERS analysis combination with SPE pre-concentration are provided.

GRAPHICAL ABSTRACT



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ABSTRACT

The article describes development and application of new SERS-active sorbents for combination of surface-enhanced Raman spectroscopy (SERS) with solid-phase extraction (SPE). These sorbents are based on aluminum oxide powder loaded with silver nanoparticles (AgNP) and have been used for analyte pre-concentration with further direct detection on sorbent surface by SERS. Proposed sorbent synthesis is very easy and inexpensive while embedding of previously prepared non-aggregated or artificially aggregated AgNP to alumina matrix allows tuning optical properties and increasing Raman spectra enhancement. Surface modification of the sorbent *via* polyelectrolyte molecules was carried out as well in order to regulate surface charge and sorption properties. Thus, described approach can be further applied for analysis of multicomponent mixtures *via* SPE separation with further SERS detection.

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1. Introduction

Surface-enhanced Raman spectroscopy (SERS) has been a subject of tremendous scientific interest for the last 40 years [1,2] because of its attractive advantages such as a very low limit of detection (close to single molecular detection [3]), multiplex analysis of multicomponent mixtures owing to narrow Raman peaks [4,5] and ability to work in aqueous environment. There are many of SERS sensors based on different platforms which are used for bioanalytical and medical purposes [6,7], environmental [8,9] and food [10] analysis, *etc*.

However, the great ability of plasmonic nanostructures to enhance Raman signal from any molecule absorbed to its surface leads to main drawback of SERS—very high sensitivity to the presence of contaminants or other undesirable molecules. For example, surface of silver or gold nanoparticles can become permanently contaminated during analysis of biofluids by proteins containing thiol group. This problem can be solved in three ways: (i) mathematical treatment of Raman results, (ii) previous modification of metal nanoparticles surface with special coatings that contain a layer of Raman marker molecules and protection and recognition layers [11,12] or (iii) preliminary separation of mixtures *via* chromatography [13–15] or extraction (*e.g.* solid-phase extraction (SPE) [16–19]). The second way works well in the case of SERS nanotags [20] which are widely used, for example, in immunoassay where SERS nanotags provide high sensitivity and selectivity but can be applied only for specific target molecules.

Combination of chromatographic separation with SERS is a less investigated field compared to analysis with application of SERS nanotags, while dilution processes and/or special equipment (*e.g.* high-performance liquid chromatographs [21]) restrict sensitivity of SERS and on-site analysis. However there are several successful examples of SERS combination with thin layer chromatography [14,15].

Unlike chromatography, SPE is more useful for combination with SERS because it provides simple separation and capability to perform analysis on-site. There are two types of SERS combination with SPE: (i) application of SPE and SERS as two independent procedures [16,17] and (ii) application of SERS-active substrate with high absorption capability for both SPE and SERS [18,19,22–24]. The first type of combination includes extraction of the target component by standard SPE procedure with consequent SERS analysis of eluted chemicals. The second type allows obtaining SERS spectra directly from a SERS-active substrate which reduces analysis time and excludes elution step. Although there are several examples of application of such sorbent-like SERS platforms, most of them have problems like small specific surface area [24], poor control of plasmonic nanoparticles size and high size distribution [18,22,23], irrational using of noble metal (pure amorphous silver has been used as sorbent [18]) or activation of “hot spots” by time consuming (hours long) drying step and application of chemically unstable materials (polysaccharides) as sorbent matrix [19,22].

Therefore, we would like to report about development and application of a new SERS-active sorbents based on Al_2O_3 loaded with silver nanoparticles (Al_2O_3-AgNP) for direct combination of SPE and SERS. There are known two types of SERS substrates with Al_2O_3 as support: (i) metal nanostructured films deposited on Al_2O_3 template and (ii) AgNP embedded to the bulk of Al_2O_3. Al_2O_3 for the first type of platforms is usually fabricated *via* anodic etching [25]. The second type of SERS platforms is less spread and is usually obtained *via* AgNP embedding during wet chemical synthesis in organic solvents [26]. However none of these SERS platforms containing Al_2O_3 are used for pre-concentration or separation purposes despite wide application of pure Al_2O_3 as chromatographic sorbent. Moreover Al_2O_3 surface can be easily modified in order to change sorption properties and increase the SPE recovery [27]. Thus, we believe the bulk loaded Al_2O_3 with metal nanoparticles is a promising composite for combination of SPE with SERS.

2. Materials and methods

2.1. Materials

Aluminum sulfate ($Al_2(SO_4)_3{\cdot}18H_2O$, ≥98%, Sigma-Aldrich), anhydrous sodium carbonate (ACS reagent, Sigma-Aldrich) and poly(sodium 4-styrenesulfonate) (~70 kDa, powder, Aldrich) were used for synthesis of aluminum oxide loaded with silver nanoparticles. Silver nitrate (ACS reagent, Sigma-Aldrich), sodium citrate dihydrate (ACS reagent, Sigma-Aldrich), sodium bicarbonate (ACS reagent, ≥99.7%, Sigma-Aldrich), sodium chloride (ACS reagent, Sigma-Aldrich), rhodamine 6G (R6G, BioReagent, Sigma) and folic acid (≥97%, Sigma) were used for synthesis of silver nanoparticles and SERS measurements. Clear water (18MΩ) was prepared by three stage purification system (UVOI-MF-1812(18)-1, CJSC “RPC MEDIANA-FILTER”, Russia).

2.2. Synthesis of silver nanoparticles

Aqueous suspensions of silver nanoparticles were synthesized *via* citrate reduction of silver ions under continuous boiling according to slightly modified Lee and Meisel method [28]. 100 mL of water was placed to 250 mL three-neck round flask with reflux condenser and boiled by heating mantle. 200 μL of silver nitrate solution (0.5 M) was added to the boiling water under vigorous stirring and kept there for 10 min, after that 100 μL of sodium citrate solution (1 M) was rapidly added to reaction mixture under continuous stirring. The mixture was boiled and stirred for 60 min and then the flask was taken from mantle and cooled down at room temperature. AgNP solution was stirred additionally for 24 h before further application in order to achieve chemical equilibrium. Final AgNP were investigated by scanning electron microscopy (SEM) and dynamic light scattering (DLS) in order to determine their size and ζ-potential.

2.3. Synthesis of aluminum oxide loaded with silver nanoparticles

AgNP embedment to aluminum oxide was performed by simultaneous addition of 5 mL of aluminum sulfate (0.2 g/mL) and 4 mL of sodium carbonate (0.12 g/mL) aqueous solutions to 20 mL of AgNP solution (sonicated before application for 5 min) under vigorous stirring. The Al_2O_3 precursors ($Al_2(SO_4)_3$ and Na_2CO_3 solutions) were added in 1 mL portions. The mixture was kept stirring for 5 min after the last portion of aluminum salt was added. Then, aluminum hydroxide with embedded AgNP was placed to 50 mL plastic tubes and centrifuged for 5 min at 2000 RPM (Eppendorf 5810R, Germany). The precipitate was rinsed once with 15 mL of water and centrifuged again. Finally, the precipitate was mixed with 10 mL of water and resuspended. This suspension was placed into a Petri dish and putted into drying cabinet for 24 h at 50 °C (SNOL 58/350 LFN, UB “UMEGA”, Lithuania). Dry samples were grinded and stored at room temperature.

In the case of sorbent modification 1 mL of poly(sodium 4-styrenesulfonate) solution (2 mg/mL) was added to the reaction mixture after addition of first portions (1 mL) of $Al_2(SO_4)_3$ and Na_2CO_3. Then the mixture was kept stirring for 5 min and after that remaining volumes of reagents (4 mL and 3 mL, correspondingly) were added. Finally, modified aluminum hydroxide loaded with AgNP was treated according to protocol described above.

In order to check repeatability, syntheses with variation of parameters (*e.g.* silver concentration, chapter 3.2) were performed