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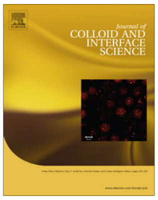

Plasmonic-polymer hybrid hollow microbeads for surface-enhanced Raman scattering (SERS) ultradetection

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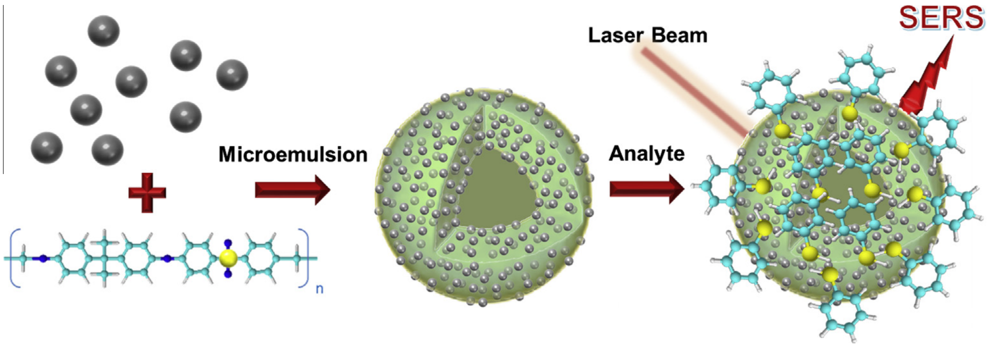
GRAPHICAL ABSTRACT



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ABSTRACT

Hybrid composites are known to add functionality to plasmonic nanomaterials. Although these substrates can be produced by common synthetic methods, the percentage of metal loaded into the functional material is usually small. Herein, we exploit a phase inversion precipitation method to incorporate large amounts of silver nanoparticles inside the polymeric matrix of polysulfone microbeads. The composite material combines the high SERS activity resulting from the plasmonic coupling of highly interacting nanoparticles and the ability to accumulate analytes of the polysulfone porous support. This allows for the quantitative SERS detection down to the nanomolar level, with a liner response that extends over an impressive concentration range of five orders of magnitude.

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1. Introduction

Surface-enhanced Raman spectroscopy (SERS) is an ultrasensitive technique for the identification of a variety of analytes [1–4]. However, since its initial discovery [5], this technique has been largely limited to qualitative and semi-quantitative applications due to the intrinsic inhomogeneities derived from the fabrication of active plasmonic materials, as well as from their largely variable and molecular-specific binding affinity for different analytes. In the recent years several works described new plasmonic platforms with the ability of reporting quantitative results. These studies are mainly based in lithographic techniques including physical evaporation with electron or ion beam patterning, nanosphere lithography or direct imprinting of plasmonic colloidal particles [6]. Despite their good performances, these methods require expensive setups for fabrication, and cannot be easily industrialized. Additionally, linearity in their optical response is limited to no more than two orders of magnitude [7,8].

To address such issues, colloidal fabrication of plasmonic substrates for SERS has evolved in different directions, such as the combination of metallic nanoparticles with non plasmonic materials acting as support or matrix. The principal goals of constructing these composite materials include the formation of stable hot spots, the increase in size of the plasmonic platform up to the micrometer scale in order to make easier their integration into sensing devices; and the development of analyte-trapping capability to concentrate the target molecule. Materials selected as support for plasmonic particles include inorganic oxides, mainly silica [9] or iron oxides [10], and polymers such as polystyrene [11]. As a matrix, the preferred materials are usually polymers including agarose [12,13], polyacrylic acid [14], polyallylamine [14], polyurethane [15], poly(*N*-isopropyl acrylamide-acrylic acid-2-hydroxyethyl acrylate) [16] or polystyrene [15], using techniques such as microfluidic flow focusing [12], or suspension [17] and living polymerization [18]. Notably, these fabrication methods give rise, on the one hand, to dense polymer structures with low porosity, thus hampering the analyte diffusion inside the matrix and, on the other hand, to low amount of trapped nanoparticles (around 1% as compared with the total weight of the material), which severely limits the extensive generation of hot spots (i.e. low SERS activity). Furthermore, the analyte diffusion to the inner parts of the microparticles may be undetected by SERS due to the limited laser penetration across the thick composite structure, leading to an underestimation of the analyte detection.

These disadvantages mainly arise from the fact that most of the fabrication methods of nanoparticle-polymer composites require the mixing of liquid phases where the solubility of the polymers is much larger than that of the nanoparticles (i.e. the nanoparticle concentration is low). On the other hand, a minimum quantity of polymer is required to form the polymer matrix, which remains much larger than the maximum tolerated nanoparticle concentration in the mixture. Furthermore, the combination of hydrophilic and hydrophobic solvents as required in some fabrication methods (i.e. microfluidics or suspension and dispersion polymerization), usually leads to colloidal instability and, thus, uncontrolled nanoparticle aggregation.

As an alternative synthetic strategy to circumvent such problems, one can relies on layer-by-layer protocols [14]. However, these methods are extremely time-consuming, especially for the fabrication of large batches of discrete microcapsules. On the contrary, phase inversion precipitation methods [19] allow to increase the nanoparticle content by reducing the amount of polymer far below the minimal concentration required by the common methods. Importantly, since the driving force to form the beads is air, highly porous hollow microparticles can be produced, thus favoring the diffusion of the analyte through the support and its positioning close/onto the plasmonic surfaces.

Herein, we present a novel synthetic strategy for the incorporation of silver nanoparticles (AgNPs) in high content within the polysulfone microbeads (PSf) of high porosity, based on the phase inversion precipitation method. As a result, these composite materials (PSf/Ag) accommodate a densely packed collection of efficient hot spots while providing large accessibility for the target molecules to the metallic surfaces, allowing for the SERS quantitative detection in a window of five orders of magnitude.

2. Experimental

2.1. Materials

Trisodium citrate, silver nitrate (99.9%, $AgNO_3$), Polyvinylpyrrolidone (PVP, Mw = 40,000), N,N-Dimetilformamida (DMF), ethanol (EtOH), and Polysulfone (PSf, Mw = 16,000) were purchased from Sigma Aldrich. All reactants were used without further purification. Milli-Q water was used in all aqueous solutions.

2.2. Synthesis of silver nanoparticles

Silver nanoparticles (AgNPs) of ca. 50 nm diameter were synthesized as follows. Briefly, 1 L of milli-Q water was heated under vigorous stirring. 6.8 mL of an aqueous solution of trisodium citrate (0.1 M) and 0.996 mL of an aqueous solution of ascorbic acid (0.1 M) were consecutively added to the boiling water. After 1 min, 0.744 mL of $AgNO_3$ (0.1 M) were also added to the mixture. The solution was kept boiling for 1 h under stirring and then left to cool down to room temperature. AgNPs were functionalized with PVP by mixing 1 L of colloids into an aqueous solution of PVP (5 g in 20 mL) to yield polymer-stabilized nanoparticles (AgNPs@PVP). The suspension was maintained under continuous stirring during 24 h at room temperature. Afterwards, the solution was centrifuged twice (7000 rpm, 30 min), the supernatant was discarded and the AgNPs@PVP sediment was redispersed in 1 mL of DMF.

2.3. Microbeads preparation

Hybrid polysulfone/AgNPs microbeads (PSf/Ag) were prepared by phase inversion precipitation method [20]. Briefly, a polymeric solution was prepared by dissolving 15% w/w of PSf in DMF (2.490 mL) followed by the addition of the AgNPs@PVP dispersion in DMF (1 mL). The final composition of the polymeric solution was 82.3% of DMF, 15% of PSf and 2.7% of AgNPs (w/w). The mixture was stirred during 24 h at room temperature. To form the microbeads, an airbrush device working in semi-continuous process with a nozzle size of 800 μm was employed [20,21] to produce microdroplets which precipitate in a coagulation bath containing 500 mL of water. Finally, the microbeads were collected by filtration using a 5 μm nylon filter and were stored under vacuum in a desiccator.

2.4. Characterization

Evolution 201 UV–Visible Spectrophotometer (Thermo Scientific) with a Hg light source and a wavelength range from 300 to 850 nm was employed to measure the absorption of silver colloids. External morphology of PSf/Ag microbeads was analyzed by JEOL JSM 6400 Scanning Microscopy Series, with acceleration voltage of 15–20 kV. Particles size distribution was determined by analyzing the SEM micrographs. Internal morphology of PSf/