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Fabrication of SERS-active structures via electrostatic deposition of colloidal gold nanoparticles on polymer microspheres

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Abstract. In the present study, we report on the fabrication and investigation of SERS active structures based on the polystyrene microspheres functionalized with gold nanoparticles. Successful deposition of the gold nanoparticles on the microsphere surface has been confirmed using the scanning electron microscopy and the zeta potential measurements. The proof-of-concept experiments have demonstrated the SERS effect with the average enhancement factor of about 10^3 . The studied structures are stable, easy to fabricate, and ready for application in sensing.

Keywords: gold nanoparticles, plasmonic nanoparticles, microspheres, surface-enhanced Raman scattering (SERS), layer-by-layer deposition

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Материалы конференции

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Изготовление SERS-активных структур методом электростатического нанесения коллоидных наночастиц золота на полимерные микросферы

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Аннотация. В настоящей работе была разработаны и исследованы SERS-активные структуры на основе полистирольных микросфер, функционализированных наночастицами золота. Успешное осаждение золотых наночастиц на поверхность микросфер было подтверждено с помощью сканирующей электронной микроскопии и измерений дзета-потенциала. В ходе предварительных экспериментов наблюдался эффект SERS со средним коэффициентом усиления около 10^3 . Изучаемые структуры стабильны, просты в изготовлении и готовы к применению в сенсорике.

Ключевые слова: золотые наночастицы, плазмонные наночастицы, микросферы, комбинационное рассеяние с усилением поверхности (SERS), послойное нанесение

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Introduction

Surface-Enhanced Raman Scattering (SERS) is a promising tool for the analysis of chemical composition and structural features of molecular and crystalline materials. The SERS method has a high selectivity for an analyte adsorbed on the surface of a plasmonic nanoparticle or located in the near field of a plasmon. For sensing applications, plasmonic nanoparticles are often assembled into more complex SERS-active structures or SERS substrates which provide higher enhancement and broader functionality [1]. Thereby, the development and fabrication of SERS-active structures from plasmonic nanoparticles have become subjects of great interest among researchers due to the high demand for ultra-sensitive detectors of environmental pollutants, pesticides, toxic or radioactive ions, and more [2].

To date, a wide variety of methods exists that allow to create SERS structures. They include direct synthesis or post-synthetic deposition of metallic nanoparticles on planar substrates and in matrices [1], nanoparticle self-assembly with the help of different stabilizing agents [3], nanostructure fabrication directly on solid substrates by nanolithography [4], and screen printing [5]. However, there is still an ongoing search for the new types of SERS structures that would be cost-effective and provide better functionality at the same time. Most of the currently available structures are two-dimensional, hence they require collection and deposition of the analyte on the planar slides. Despite common use, this approach might not be the best option for some scenarios, especially in biology, where the study of fluids is frequently performed. For these purposes, three dimensional SERS structures are more suitable, such as nanoparticle-decorated hollow fibers [6], membranes [7], and microspheres [8], that allow direct investigation of the analytes in liquid samples. Furthermore, three-dimensional architecture can provide larger Raman signal enhancement due to additional contribution from the plasmonic hotspots located in various places along the z-axis within the excitation focal volume.

Polymer microspheres (PMS) can be effectively used as the three-dimensional supports for plasmonic nanoparticles. Three approaches can be used to prepare microspheres covered with nanoparticles: (1) *in-situ* nanoparticle synthesis in the presence of microspheres [9]; (2) polymerization in the presence of nanoparticles [8]; (3) self-assembly of nanoparticle layers on the microsphere surface *via* electrostatic layer-by-layer deposition [10]. The latter approach can be very promising as it enables formation of dense nanoparticle layers with high reproducibility. In this method, oppositely charged polyelectrolytes (PE) are deposited on the surface of the PMS to produce a smooth charged coating which electrostatically attracts nanoparticles from the solution. This method has already been successfully used to deposit colloidal quantum dots and gold nanoparticles (AuNPs) on the surface of the PMS for applications in cytometry and catalysis [10, 11]. However, the possibilities of utilizing such structures for the SERS-based applications have not been widely considered.

The goal of this research is the formation of SERS-active structures from commercially available polystyrene microspheres and colloidal gold nanoparticles *via* electrostatic layer-by-layer deposition. A high stability of the prepared structures was achieved by precoating the microspheres with multiple PE layers and by using thiols as stabilizing ligands for AuNPs. The proof-of-concept measurements of the organic dye (pseudoisocyanine iodide) Raman spectra revealed that the AuNP-coated PMS structures provide sufficient enhancement and can be used in the field of SERS-based sensing.

Materials and Methods

Materials. Chloroauric acid (99.995%), trisodium citrate, pseudoisocyanine iodide (97%), 3-mercaptopropionic acid (99%) (MPA), poly(sodium 4-styrenesulfonate) ($M_w \sim 70,000$) (PSS),

poly(allylamine hydrochloride) ($M_w \sim 50,000$) (PAH) were purchased from Sigma Aldrich. Polystyrene microspheres (carboxylated, 4 μm in diameter) were obtained from Kisker Biotech. Deionized water (conductivity < 6 mS/cm) was used throughout the experiments.

Synthesis of AuNPs and ligand exchange. The synthesis of colloidal gold nanoparticles was carried out by the common citrate reduction method described in the reference [3]. After the synthesis, the ligand exchange procedure on AuNPs with mercaptopropionic acid was carried out according to the following protocol. First, a solution of MPA (10^{-5} M) was prepared in water with pH ~ 10 – 11 adjusted by NaOH to deprotonate the thiol groups. This solution was then added to AuNPs, and the obtained mixture was vigorously stirred for 20 minutes at room temperature, followed by addition of acetone and centrifugation. Finally, a purple-colored precipitate containing MPA-capped AuNPs was redissolved in pure water.

Preparation of AuNP-coated PMS. The electrostatic layer-by-layer deposition technique was adapted from the reference [11]. The first step of the standard protocol is the deposition of a smooth positively charged coating on the surface of carboxylated microspheres. This preliminary coating is composed of the three layers of polyelectrolytes added sequentially: PAH, PSS, PAH. Each layer was deposited by mixing a solution of homogenized suspension of PMS and a corresponding polyelectrolyte (3 mg/ml) in a 0.5M NaCl solution. After stirring the mixture for 20 minutes at room temperature, three centrifugation/washing cycles were performed to remove excess PE, followed by a final redispersion of PMS in water. The PE deposition and washing procedure was repeated until the PMS with three layers (PAH/PSS/PAH) were formed. For the deposition of AuNPs, the solution of MPA-capped AuNPs was added to the obtained suspension of microspheres with three layers of PE and stirred for 24 hours. The resulting suspension was washed three times to remove the unattached nanoparticles.

Equipment. The UV-VIS absorption spectra were recorded using a UV-Probe 3600 spectrophotometer (Shimadzu, Japan). Scanning electron microscopy (SEM) images were obtained on Merlin (Zeiss, Germany) by depositing samples on silicon substrates. Measurements of Raman spectra were performed with a confocal Raman microscope inVia (Renishaw, United Kingdom). Raman spectra were excited at 514 nm and recorded using a 50 \times objective lens. SERS mapping was performed using 1995 points per sample area ($35 \times 55 \mu\text{m}$) with an exposition time of 1 s per point. The hydrodynamic diameter and the zeta potential measurements of the AuNPs and the microspheres were performed on Zetasizer Nano (Malvern, United Kingdom).

Results and Discussion

In this work, gold nanoparticles were selected for the fabrication of SERS structures because of their high stability, ease of production, and suitable energy position of the plasmonic band [12]. In the common synthesis of AuNPs, chloroauric acid is reduced to gold with the help of sodium citrate in the aqueous medium [3]. Citrate ions work as stabilizing agents for the synthesized nanoparticles, favoring their long-term colloidal stability. However, during preliminary experiments we have found that the deposition of the as-prepared citrate-capped AuNPs on the microsphere surface results in instability and aggregation. It is plausible, that the weakly bound citrate ions detach from the nanoparticle surface in the presence of the functional groups of polyelectrolytes (i.e., amines, as the outer PE shell consists of PAH), leading to the uncontrollable cross-linking between AuNPs and microspheres. Therefore, to create uniform layers of nanoparticles on the surface of microspheres, we have performed the ligand exchange on AuNPs with 3-mercaptopropionic acid. As expected, the stronger bond between the metal and the thiol group of MPA significantly reduces the possibility of ligand detachment and prevents the system from aggregation.

The absorbance spectrum and the SEM image of the AuNPs prior to deposition on the PMS surface are shown in Fig. 1. As seen in Fig. 1, *a*, gold nanoparticles exhibit a plasmonic band at 525 nm, consistently with the other reports. Based on the particle size distribution obtained from the SEM images (see Fig. 1, *b*), the average size of AuNPs was estimated to be 22 ± 3 nm. The hydrodynamic diameter and the zeta-potential measurements revealed that the nanoparticles were well-dispersed and had an average zeta potential of ca. -25 mV, indicating a net negative charge due to the ionized carboxylic groups of the organic stabilizing shell.

Polystyrene microspheres are cheap, robust, and possess narrow size distribution. Therefore, we have selected them as the three-dimensional supports for the fabrication of SERS-active structures.

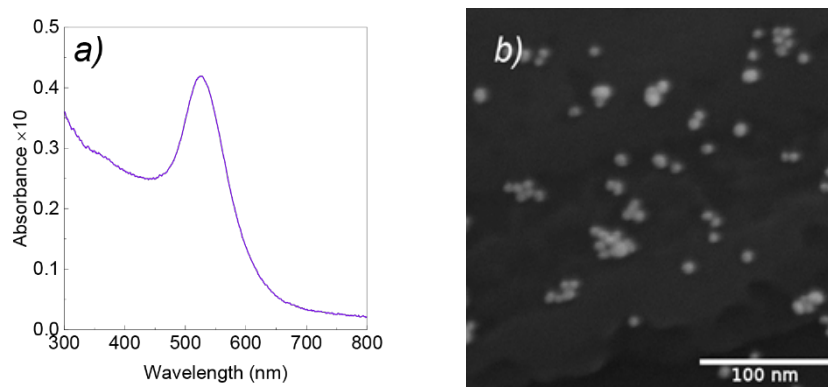


Fig. 1. Absorbance spectrum of the AuNPs solution with a plasmonic band at 525 nm (a); The SEM image of AuNPs (b)

For nanoparticles to be assembled on the microsphere surface by electrostatic forces, the components must have strong opposite charges. According to previous reports, at least three polyelectrolyte layers are necessary to facilitate a denser packing of PE and provide a stable charge on the PMS surface [13]. Since the carboxylate-modified polystyrene microspheres bear a negative charge, the first deposited layer was a positively charged polyelectrolyte PAH. Next, two more layers of the oppositely charged polyelectrolytes (PSS and PAH) were deposited in accordance with the protocol, so that the outer coating is charged positively. The average value of the zeta potential for the PMS with three layers of PE was ca. +45 mV measured directly after the deposition of the final layer. This value retained for at least one week after the coating procedure, which demonstrates a good stability of the polyelectrolyte layers.

Next, the MPA-capped AuNPs were self-assembled on the surface of the positively charged microspheres in a same manner as polyelectrolytes. The utilization of MPA as a strong stabilizing agent for gold nanoparticles ensured that the electrostatic interaction is primarily responsible for the deposition of AuNPs. After purification from the unbound nanoparticles, the functionalized microspheres were characterized by scanning electron microscopy and zeta-potential measurements.

Fig. 2 shows a SEM image of the PMS-AuNP structures, where AuNPs can be observed on the surface of the microspheres. As seen from the SEM image, the nanoparticle coverage is relatively sparse, which might be due to low nanoparticle concentration used during the assembly process. At the same time, the zeta-potential values of the prepared structures showed a significant shift from ca. +45 mV to ca. -10 mV (not shown). This demonstrates a successful adsorption of AuNPs on the PMS surface. It is also worth noting that the prepared AuNP-coated microspheres remained stable and retained negative zeta potential for more than a week.

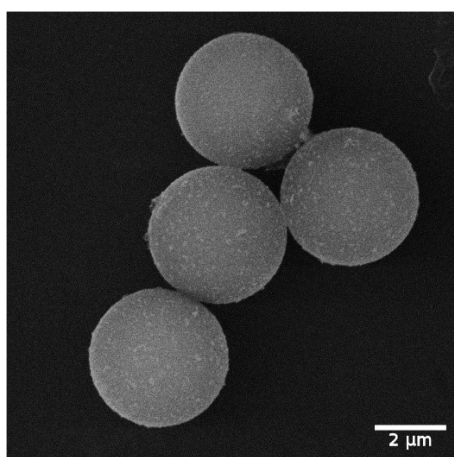


Fig. 2. SEM image of the PMS/PAH/PSS/PAH/AuNP structures

drop-casted on top of it. Then, the Raman scattering map for the 1365 cm^{-1} dye band was recorded. As seen from Fig. 3, a, the intensity enhancement is observed in those regions where the nanoparticle-decorated microspheres are located.

For further analysis, we measured the Raman spectra of the pure dye, as well as in the presence of PMS with and without AuNPs on the surface, respectively (Fig. 3, b). As follows from Fig. 3, b, only the spectrum corresponding to the sample with the PMS-AuNP structures clearly shows the characteristic dye Raman band at 1364 cm^{-1} . This band is absent in other spectra, which

confirms the enhancement effect. To estimate the efficiency of our structures, we have calculated the analytical enhancement factor (AEF) [14]:

$$AEF = \frac{I_{SERS}}{I_R} \cdot \frac{c_R}{c_{SERS}}, \quad (1)$$

where I_{SERS} and I_R are the intensities of the dye, with and without AuNPs, respectively, and c_{SERS} and c_R are the concentrations of the dye, with and without AuNPs, respectively.

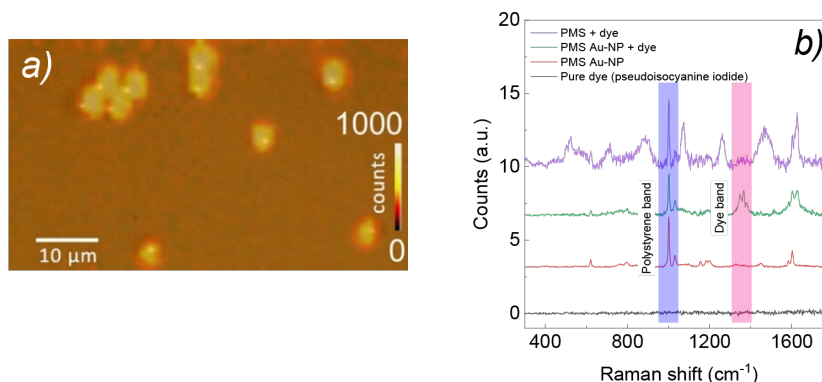


Fig. 3. Raman scattering intensity map recoded for 1365 cm^{-1} band of pseudoisocyanine iodide (a); A set of Raman spectra demonstrating the SERS effect of the prepared PMS-AuNP structures (b)

The value of AEF calculated using equation 1 has the order of ca. 10^3 . These values are somewhat lower than those reported for other SERS-active structures [15]. This indicates the need to improve the synthesis to reach a more compact packing density of gold nanoparticles.

Conclusion

In the present work, we have fabricated three-dimensional SERS-active structures by coating polymer microspheres with three layers of polyelectrolytes followed by the electrostatic deposition of AuNPs from aqueous solutions. We have characterized the morphology of the prepared structures and estimated the Raman scattering enhancement by using pseudoisocyanine iodide as an analyte. The analytical enhancement factor on the order of 10^3 has been reached, which is comparable to more complex SERS structures. The fabrication procedure is easy to upscale, and the prepared samples remain stable for more than a week. This opens wide possibilities for using such structures in analytical and sensing applications.

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