HEXAGONALLY ORDERED GOLD SEMISHELLS AS TUNABLE SERS SUBSTRATES

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Abstract

The spectroscopic technique based on surface-enhanced Raman scattering (SERS) has attracted considerable scientific interest due to the combination of its extreme sensitivity, in certain cases reaching single-molecule detection limits, and the specificity of Raman spectra. For molecules adsorbed on noble metal nanostructures, Raman signal enhancement of several orders of magnitude can arise as a result of localized surface plasmon resonance (LSPR). This effect can be observed when the frequency of light irradiating the metal surface matches the resonant frequency of conduction electrons in the nanostructure. Since this frequency is determined by the geometry and size of the nanostructure, it may be intentionally shifted to the spectral range suitable for specific applications. However, the use of SERS in many applications is limited by the properties of the nanostructure surfaces, so-called SERS substrates, especially by the insufficient homogeneity of the enhancement. Using self-assembled dielectric spheres as templates, we prepared periodic SERS substrates, composed of hexagonally ordered gold semishells, which provide both high and homogenous enhancement over the whole surface. The functionality of our substrates was verified by measuring SERS spectra of methylene blue at very low concentrations. The LSPR frequency of the semishells may be tuned by several parameters, such as its height, thickness of the gold shell etc. We propose a method based on template-assisted self-assembly which enables the precise control over the semishell geometry and paves the way to the preparation of rationally designed semishell arrays with optimal parameters.

Keywords: Surface-enhanced Raman scattering (SERS), tunable SERS substrate, template-assisted self-assembly, semishell.

1. INTRODUCTION

The spectroscopy based on surface-enhanced Raman scattering (SERS) [1-3] is a widely studied method due to its molecular specificity, ensured by Raman scattering, and very low detection limits, in certain cases reaching single-molecule level [4]. Raman signals of molecules adsorbed on a noble metal nanostructured surface can be enhanced by several orders of magnitude as a result of the excitation of localized surface plasmon resonance (LSPR) in the structure. This phenomenon can be observed when the frequency of light irradiating the metal surface is close to the resonant frequency of conduction electrons in the nanostructure. Since this frequency is determined mainly by the material, geometry, and size of the nanostructure, it may be tuned to the desired spectral range.

Nanostructures consisting of a thin metallic shell and a dielectric core, so-called nanoshells [5], have been widely studied due to the possibility to shift the LSPR frequency from visible to NIR simply by varying the ratio of the inner to the outer nanoshell radius. However, it has been shown that open shell nanostructures, such as semishells [6], can be tuned even more easily (because their height represents an additional degree of freedom) and at the same time can produce higher enhancement of the local electromagnetic field around the rim of their apertures [7]. They also display other interesting optical properties, such as different scattering angular dependence for two distinct dipolar bonding modes (axial and transverse) [8].
Although the applications of SERS for trace detection in biochemistry, diagnostics, or food safety have long been predicted, its use is still limited by the properties of the SERS substrates, i.e. nanostructured surfaces which cause the Raman signal enhancement. One of the issues is the insufficient homogeneity of the enhancement over the surface of conventionally used substrates, such as aggregated colloidal particles or electrochemically roughened surfaces. However, this problem can be solved simply by fabricating a periodic surface. Among the fabrication methods, self-assembly is particularly advantageous due to its low cost and high throughput. Its major disadvantages, the occurrence of defects and lack of arrangement variability, can both be minimized by using pre-structured templates.[9]

Recently we have reported on the fabrication of periodic arrays of metal semishells [10]. In this paper, we demonstrate their improved SERS performance after adding one short step to the fabrication procedure, and we propose a method based on template-assisted self-assembly which enables the control of all parameters affecting the LSPR frequency of the semishell: its diameter, height (more precisely, fractional height), metal shell thickness, distance from surrounding semishells, and material.

2. EXPERIMENTAL

2.1 Preparation of close-packed gold semishell arrays
The hexagonally ordered array of close-packed gold semishells on a poly(dimethylsiloxane) (PDMS) substrate was prepared as described previously [10]. Aqueous dispersions of polystyrene (PS) microspheres with diameters (253 ± 8) nm, and (535 ± 16) nm, were purchased from microParticles GmbH (Berlin, Germany); thin gold layers were prepared by magnetron sputtering deposition on the PS templates in Cressington 208HR high-resolution sputter coater; PDMS was purchased as Sylgard® Elastomer Kit 184 from Dow Corning. The gold semishell arrays were subjected to oxygen plasma etching in SPI Plasma Prep™ III Plasma Etcher for 2 min.

Obtained substrates were then dipped in solution of methylene blue (pH 3.6, concentration 10⁻⁷ – 10⁻⁹ M) for 1.5 hour and dried in nitrogen flow.

2.2 Template-assisted preparation of gold semishell arrays
Aqueous dispersions of polystyrene (PS) microspheres with diameters (152 ± 7) nm, (535 ± 16) nm, and (920 ± 23) nm, were purchased from microParticles GmbH (Berlin, Germany). Highly diluted water-ethanol dispersions of the spheres were repeatedly drop-casted onto pre-structured templates. As a template for spheres with the diameter 920 nm, a regular grating fabricated by interference photolithography was used; a negative poly(methyl methacrylate) (PMMA) replica [11] of structures on cicada (Cryptotympana aquila) wing sputtered with 40 nm of gold served as a template for the spheres 152 nm in diameter. Both templates consisted of cylindrical hole arrays; the grating was hexagonal with periodicity 1.5 µm and hole diameter 700 nm, the cicada negative replica displayed quasi-hexagonal ordering with holes cca 100 nm in diameter. Except for the self-assembly process, all steps leading to the gold semishells were performed as described in section 2.1.

2.3 Characterization
Samples were characterized by scanning electron microscope (SEM) JEOL JSM-7500.

SERS spectra of methylene blue (MB) were measured on the confocal Raman microspectrometer LabRam HR800 (Horiba Jobin-Yvon) with a nitrogen cooled CCD detector, using 633 nm excitation line (He-Ne laser), objective 100×, and accumulation time 1 × 10 s. The laser power at the sample was cca 0.2 mW.
3. RESULTS AND DISCUSSION

3.1 Close-packed gold semishell arrays

It was hypothesized that the SERS activity of periodic arrays of gold semishells [10] might be impaired due to a thin layer of PS remaining at the semishell bottom and disabling the adsorption of molecules onto the gold surface. Longer exposure of PDMS substrate to toluene could lead to swelling so it was chosen to remove the remaining PS by oxygen plasma etching.

The prepared array of hexagonally ordered 20 nm thick gold semishells (253 nm and 535 nm in diameter) after being subjected to plasma etching is shown in Fig. 1. The SERS activity of these nanostructures was verified by measuring spectra of MB and compared to our previous results [10]. The comparison reveals that SERS signals are almost one order of magnitude stronger after the plasma etching; the detection limit was estimated to be less than $10^{-8}$ M. Moreover, the obtained spectra were very reproducible, as is illustrated in Fig. 2 on ten SERS spectra of MB collected from 10 randomly chosen spots at one sample of close-packed semishells 253 nm in diameter. All spectra are baseline corrected.

Fig. 1: Prepared array of close-packed gold semishells 253 nm (left) and 535 nm (right) in diameter.

Fig. 2: SERS spectra of MB measured at ten randomly chosen spots on close-packed gold semishell array (MB concentration $10^{-7}$ M).
3.2 Controlling the semishell shape

When two PS spheres are in contact, they can connect and form mutual junctions. During magnetron sputtering, the sputtered metal particles overlay the pattern defined by the junctions, and hence form a “lace-like” rim of the semishell (see Fig. 3 left). To obtain particles with a straight rim, non-close-packed arrays of spheres should be used. An example of such a semishell, prepared by sputtering of 70 nm of gold onto a glass substrate with randomly distributed PS spheres, is shown in Fig. 3 right. The gold layer in proximity to the rim of the semishell was probably too thin to withstand the forces during the dissolution of the PS, and it was slightly bended inwards. Another disadvantage of such a preparation method is the inability to control the semishell fractional height, which determines to a large extent both the LSPR frequency and local field enhancement [7].

Using pre-structured templates with cylindrical holes enables us to control the fractional height, as well as other parameters affecting the LSPR frequency by choosing the optimal hole diameter and separation. During the deposition onto such templates, the PS spheres are dragged into the holes by capillary forces and form a non-close-packed arrangement with well defined spacing.

Fig. 4 left shows a PS sphere 920 nm in diameter, which has been dragged into a hole in the hexagonal grating, coated with 40 nm of gold; Fig. 4 (right) shows three semishells with aperture sizes determined by the grating hole dimensions, respecting the periodicity of the hexagonal template. Although the gold shell is much thinner than on Fig. 3 right, it was not distorted during the dissolution of PS and the aperture dimensions correspond to the diameter of the holes in the template.

The arrangement of smaller PS spheres, 152 nm in diameter, on negative cicada wing replica is illustrated in Fig. 5 (left). The particles imitate the quasi-periodic ordering of the template, creating close-packed structures in certain cases and separated semishells in the others. The height of the semishell obtained in this configuration is clearly visible in Fig. 5 right, which depicts an individual gold-coated particle removed from the hole during manipulation with the sample.

Fig. 3: The shape of individual semishells, 535 nm in diameter, in close-packed (left) and non-close-packed arrangement (right).
Fig. 4: Template-assisted preparation of non-close-packed 40 nm thick gold semishells 920 nm in diameter using a hexagonal grid (left), semishells on PDMS respecting the arrangement of the grating (right).

Fig. 5: Template-assisted preparation of 40 nm thick gold semishells 152 nm in diameter using the negative cicada replica (left), individual semishell before removing the PS sphere (right).

4. CONCLUSION

Ordered arrays of gold semishells represent a promising substrate for spectroscopy based on SERS due to their high enhancement and the ability to tune the LSPR frequency over a broad spectral range by varying one of several geometrical parameters, such as height, diameter, and shell thickness. By measuring SERS spectra of methylene blue for concentrations down to $10^{-8}$ M, we have verified that gold semishells in close-packed arrangement can serve as a highly reproducible SERS substrate with both sufficiently high and homogeneous enhancement over the whole periodic surface. Moreover, we introduced a template-assisted technique which enables a precise control over all parameters affecting the LSPR frequency, and hence could be used to prepare a rationally designed SERS substrate with optimal geometry providing the maximum enhancement of the local electromagnetic field.
ACKNOWLEDGEMENTS

L. Š. is very grateful to D. Najdek, J. Svoboda, and M. Květoň for the fabrication of the hexagonal grating, to J. Berger for the fabrication of the negative replica of structures on cicada wings, and to M. Kalbač for performing the plasma etching procedure. This work was supported partially by grants GAAV KAN401220801, Ministry of Education, Youth and Sports, and project COST OC09038.

LITERATURE