

ORDERED METALLIC NANOSTRUCTURES FOR SURFACE- ENHANCED RAMAN SPECTROSCOPY

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Abstract. In the present paper scanning electron microscopy in combination with vis-nir transmission and reflectivity spectroscopy have been applied to characterize the optical and structural properties of the gold film deposited on periodic corrugated surfaces of polystyrene colloidal crystal. The SERS spectra of Rhodamine 6G 10^{-4} M methanol solution have been also recorded by using the 514 and 633 nm laser lines for excitation to test the SERS properties of this substrate.

Key words: ordered gold nanostructures, SEM, vis-nir transmission, reflectivity, SERS measurements

1. INTRODUCTION

Surface-enhanced Raman spectroscopy (SERS) is a well-established method, which allows the detection of organic molecules adsorbed on metal substrates (silver, gold, copper) at submicromolar concentration. SERS phenomenon can enhance Raman signals of adsorbed nonresonant molecules by 5 to 6 orders of magnitude. In certain cases, however, the enhancement can be enormous. Several experiments have demonstrated that the SERS enhancement can approach 10^{14} to 10^{15} , and thus enable the detection of a single molecule [1].

The large enhancement of the Raman scattering intensity has been explained by means of two mechanisms: the electromagnetic mechanism attributed to the increase of the local electromagnetic field of the adsorbate because of the excitation of the surface plasmons on the metal surface, and the chemical adsorption mechanism, which is attributed to short distance effects due to the charge transfer between the metal and the adsorbed molecule [2].

A wide variety of substrates has been found to exhibit SERS. Typical SERS substrates, such as roughened gold and silver electrodes or colloidal aggregates, are disordered and often produce unpredictable signal enhancements. Moreover, their structures are unstable and quickly lose their SERS activity. Various metallic nanostructures have been developed and investigated as SERS-active solid substrates, including roughened metal electrodes, metal island films, metal-coated nanosized posts, spherical gold nanoshells, subwavelength binary gratings, pyramidal silver islands, colloidal metal films

and silver-coated nanospheres arrays [3]. Both experimental and theoretical studies on SERS effect indicate that the magnitude of enhancement of Raman signal is highly dependent on the nanometer-scale morphology, i.e. nanoparticle size and interparticle distance [4]. For that reason, controlled methods for preparing nanostructured metallic substrates would provide more useful correlations between surface structure, optical properties and signal enhancement [5]. Additionally, it would be highly desirable to be able to tune the substrate surface plasmon resonance wavelength in the way the substrate surface plasmon resonance (SPR) could be matched to the fixed wavelengths of economical and readily available laser sources.

In the present work we investigate the structural and optical properties of a new class of metallic nanostructures with the major goal to control and manipulate its potential for SERS active-substrates. By using these nanostructures, which consist of corrugated gold films deposited on top of highly ordered arrays of polystyrene nanospheres [6], we were able to record good SERS spectra of a submonolayer of Rhodamine 6G (Rh6G) adsorbed on the gold film by using the 514 and 633 nm excitation lines.

2. EXPERIMENTAL

Sample and substrate preparation. Rhodamine 6G and all materials involved in sample and substrate preparation were purchased from commercial sources as analytical pure reagents. For recording the SERS spectra Rhodamine 6G 10^{-4} M methanol solution was used.

The SERS substrate was prepared according to the drop-coat method of nanosphere ordering as described in literature [7]. The solid substrate (silica of dimensions 25 mm x 25 mm x 1 mm) was treated by etching in a solution of 3:1 $H_2SO_4:H_2O_2$ for a period of 2 hours, washed in deionised water, immersed in a solution of 5:1:1 $H_2O:NH_4OH:H_2O_2$ and sonicated in an ultrasonic bath for 1/2 hour. Firstly, a suspension of polystyrene nanospheres of 220 nm diameter was drop-coated onto the substrate where they, after water evaporation, self-assembled into hexagonally close-packed two-dimensional (2D) colloidal crystals. Then, the substrate was mounted into the vacuum chamber of a vapour deposition system and gold films of 64 nm thickness were thermally evaporated onto the substrate under a pressure of 5×10^{-6} Torr.

Experimental measurements. Scanning electron microscopy investigations were performed with an JEOL electronic microscope. Transmission and reflectivity spectra were measured at normal incidence using a Perkin Elmer Lambda 9 uv-vis-nir spectrometer.

The SERS measurements were performed on a Dilor Labram system by using an Olympus LMPlan Fl 50 microscope objective and two laser lines for excitation (514 nm and 633 nm respectively). The FT-Raman spectrum of Rhodamine 6G was recorded with a Bruker IFS 120HR spectrometer equipped with a FRA 106 Raman module and a Nd:YAG laser for excitation with the 1064 nm line.

3. RESULTS AND DISCUSSION

The microstructure of the sample was studied by scanning electron microscopy (SEM). Figure 1 shows the SEM image of the surface of the sample. A “polycrystalline”

structure of the nanospheres assembly was observed. The ordered domains range from a few to tens of μm . It can be seen from the pattern of the ordered arrays that the nanospheres packed either in square or hexagonal close-packed structure. The voids between beads and the beads surface was completely filled and, respectively, coated with metal. Depositing a thin film of metal over the nanospheres produces interconnected metallic nanoparticle array. The extend of coating increased with the metal film thickness.

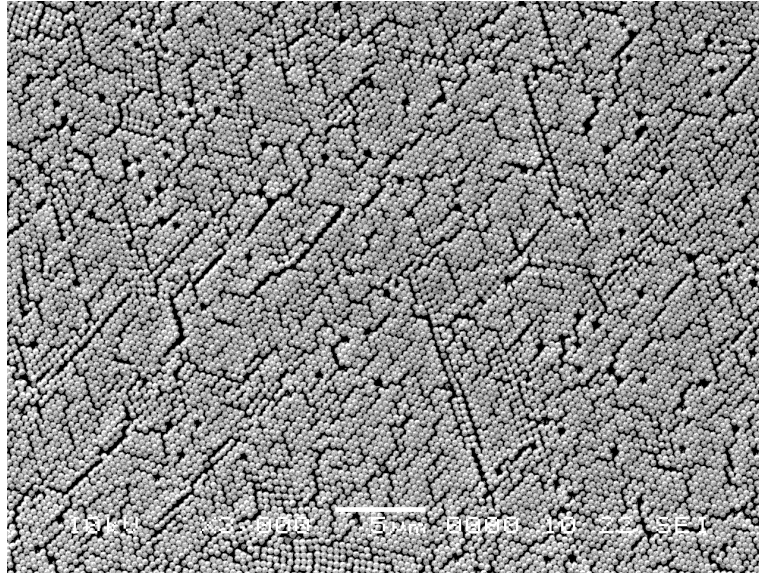
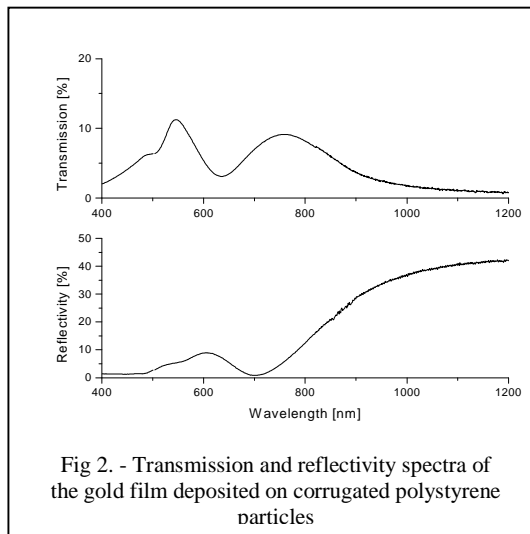


Fig 1. - SEM image of typical crystalline assemblies of 220 nm polystyrene nanospheres coated with gold film of 64 nm thickness.



In order to optically characterize these structures, light transmission and reflection measurements were performed at normal incidence (see Fig. 2). As a single domain area can not accommodate the whole light beam (of about 3 mm^2 cross section), we mention that our optical spectra integrate optical response of many regular microstructures and therefore give only an area-averaging information. The spectra reflect the interplay between the optical response dominated by localized surface plasmon (LSPR) modes associated with each individual

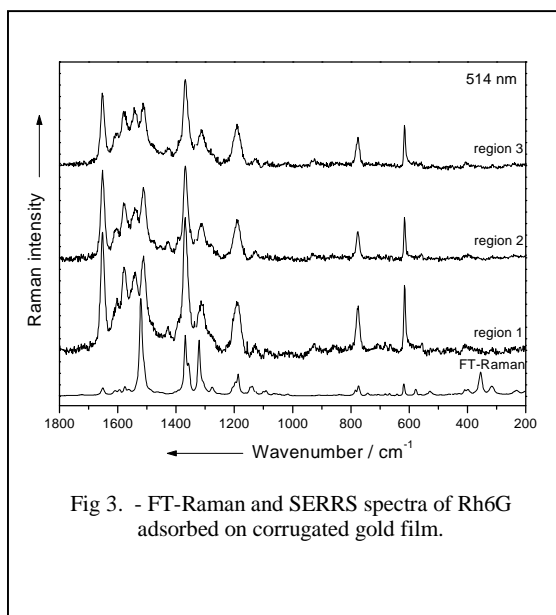
nanoparticle and modes associated with corrugated film. The vis-nir transmission and reflectivity spectra show the presence of collective surface plasmon interactions indicating SERS activity.

Table 1

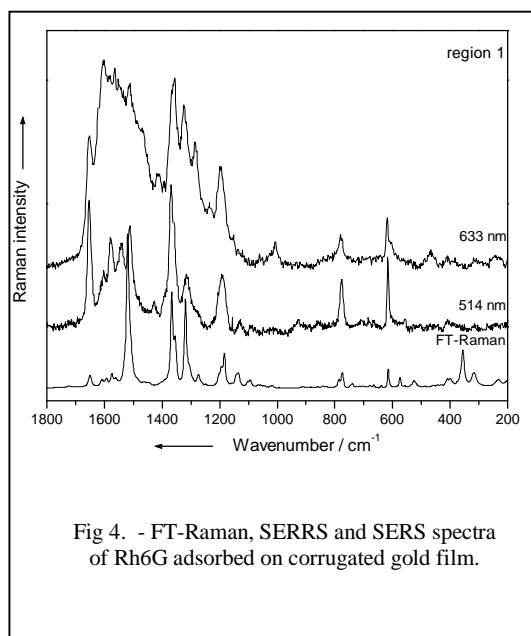
Selected observed bands in FT-Raman and SERS spectra of Rh6G with their assignment.

FT-Raman	SERRS	SERS	SERRS [8]	Assignment
614m	618m	620m	613s	$\delta(\text{CC})_{\text{ip}}$
771m 1012vw	777m	778m 1009m	776m	$\delta(\text{CH})_{\text{op}}$
1132w 1181m	1132w 1192m	1198s	1124w 1187m	$\delta(\text{CH})_{\text{ip}}$
1273w		1289ms		$\nu(\text{COC})$
1317s	1320m	1329s	1312m	$\nu(\text{CC}) + \nu(\text{CN})$
1364s	1368s	1360s	1363s	$\nu(\text{CC}) + \nu(\text{CN})$
1518s 1559vw	1512s 1543ms	1515s 1556s	1509s	$\nu(\text{CC})$
1572w 1607vw	1577ms 1603m	1569s 1606s	1572m	$\nu(\text{CC})$
1649w	1655s	1651s	1650s	$\nu(\text{CC})$

Abbreviations: m=medium, s=strong, w=weak, ms=medium-strong, ν =stretching, δ =deformation, ip=in-plane, op=out-of-plane



potential of this SERS-active substrate. By inspecting Fig. 1 one can observe that the spectra collected from different sites of different ordering degrees and domains areas resemble each other. Previous theoretical studies [9] on aggregate structures suggest that



It is well known [8] that Rh6G exhibits an electronic absorption maximum at 525.5 nm. Therefore, both resonance and surface enhancements are expected to contribute to the observed SERS spectra recorded with the 514 nm laser line. The SERS spectra of Rh6G adsorbed on corrugated gold film recorded from different sites are illustrated in Fig. 3 along with the FT-Raman spectrum of the polycrystalline sample. The observed Raman and SERS bands with their assignment, which was done according to the already published data, are summarised in Table 1. Our experimental data are in good agreement with the existing results and demonstrate the great

the electromagnetic field effects responsible for SERS on solid substrates are localised in the interstitial regions of the arrays, and are accompanied by field depletion outside of these areas. The resonant excitation produce giant local fields corresponding to Raman enhancement factors of the order of 10^{11} or more [4]. This implies that the majority of the SERS signal measured from our sample is due to the excitation of very small percentage of adsorbate situated at these interstitial sites, and the individual enhancements are greater the surface-averaged values. Having in mind that the substrate shows an electronic absorption maximum around 633 nm we checked if SERS spectra could be obtained by using the economical and commercial 633 nm laser line

for excitation. The SERS spectrum of Rh6G recorded with the 633 nm line, presented together with the SERRS and FT-Raman spectra in Fig. 4, demonstrates the great capability of this substrate to provide SERS enhancements, when various laser lines are employed for excitation. The differences evidenced between the SERRS and SERS spectra can be explained by considering the resonant contribution to the overall SERS enhancement.

4. CONCLUSIONS

In this paper we have demonstrated that corrugated gold films, deposited on top of highly ordered arrays of polystyrene nanospheres, can find applications as valuable SERS substrates. Besides of their simple means of preparation, the film can be successfully used as active SERS substrate for two different excitation lines. Such features enhance their potential value for chemical and biochemical sensing.

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