Pis'ma v ZhETF, vol. 74, iss. 6, pp. 343 – 345 © 2001 September 25

Raman scattering enhancement using crystallographic surface of a colloidal crystal

S. V. Gaponenko[1)], *A. A. Gaiduk, O. S. Kulakovich, S. A. Maskevich*[+], *N. D. Strekal*[+], *O. A. Prokhorov*[*], *V. M. Shelekhina*[*]

Institute of Molecular and Atomic Physics National Academy of Sciences of Belarus, 220072 Minsk, Belarus

[+] *Ya. Kupala Hrodna State University, 230023 Hrodna, Belarus*

[*] *Institute for Powder Metallurgy, 220600 Minsk, Belarus*

Submitted 7 August 2001

Deposition of coinage metals on a crystallographic surface of a colloidal crystal is proposed to fabricate metal surface with a regular relief on a scale of 200–300 nm to get strong surface enhanced Raman scattering (SERS). The approach is performed by means of a thin gold film deposition on a surface of a crystal consisting of silica globules. Mitoxantrone molecules, a DNA intercalator, have been used to prove high SERS efficiency of the structures proposed. As compared to other SERS active substrates, metal-dielectric colloidal crystal structures possess well-defined surface parameters (globule diameter and film thickness), high stability and reproducibility. These advantages are important for systematic analysis of SERS mechanisms in mesoscopic structures and its application in single molecules detection.

PACS: 33.20.Fb, 68.43.Pq, 81.16.-c, 82.70.Dd, 82.80.Gk

Strong enhancement of Raman scattering of light by molecules adsorbed at surfaces of coinage metals (Au, Pt, Ag, Ni) with a complicate nano-relief as compared to solutions and flat dielectric surfaces (so-called surface enhanced Raman scattering, SERS) is extensively investigated during more than two decades ([1 – 3] and refs. therein). A description of this complex phenomenon in spite of an extensive research is far from being complete. Recent pioneering experiments on single molecule detection by means of SERS [4, 5] showed that local Raman scattering enhancement factor in metal-dielectric structures can be as large as 10^{14}. These findings did stimulate further experimental studies of interaction of electromagnetic field with metal colloidal [6], fractal [7], periodic surface structures [8], as well as with metal nanoshells [9]. A serious obstacle in systematic SERS research, its quantitative description and practical applications is absence of reliable techniques which allow for fabrication of reproducible and well-defined SERS active substrates with homogeneous size and shape of metal nanoparticles. Etched metal electrodes, island films, isolated colloidal particles, their small and larger fractal clusters and other metal-dielectric structures with irregular nano-relief and complicate topology are being used in SERS experiments. Each of these SERS active structures features spatial inhomogeneities which are hard to be described mathematically and reproduced experimentally. Because of uniqueness of every structure, a systematic analysis of data reported by different groups and their comparison with model theoretical calculations become ambiguous. In spite of challenging opportunities of SERS in single molecule detection, further research is necessary for understanding of underlying physical processes an its practical applications.

Several groups outlined pronounced SERS effect for molecules adsorbed at metal surfaces with regular displacement of islands, rods or globules [2, 10, 14]. In this case, SERS can be described in terms of the model in which 10^6-fold enhancement occurs due to excitation of surface plasmons [11, 12]. Resonant enhancement of Raman scattering was reported at specific laser wavelength for a given metal particles size [13]. Therefore for highest SERS efficiency a regular two-dimensional arrangement of monodisperse metal islands or globules is desirable. Though monodispersity can be achieved by means of size fractionating and using nanoshells over monodisperse colloidal globules, spatial ordering of structures remains to be performed by other means. To fabricate periodic SERS active substrates nanolithography has been proposed [14] providing superior SERS response. This technique however is rather complicate, expensive and includes specific processes which can not be reduced to chemical processing.

In the present letter, we propose to fabricate SERS active periodic metal-dielectric two-dimensional nanostructures by means of metal deposition on a crystallo-

[1)] e-mail: gaponen@imaph.bas-net.by

graphic surface of a colloidal crystal and report on the first observation of the pronounced Raman scattering enhancement at a colloidal crystal surface.

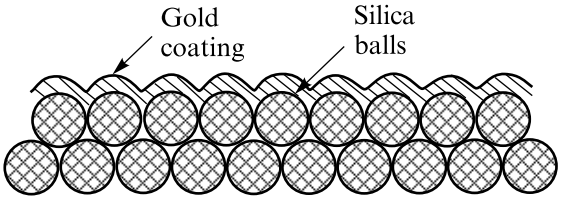

Fig.1. A schematic of periodic metal-dielectric structures formed by means of gold deposition on silica colloidal crystal surface

In the experiments, colloidal silica crystals were used developed by means of centrifugation of monodisperse silica sol with the mean particle diameter variable in the range of 200–500 nm. Similar structures fabricated by means of sedimentation have been used earlier as model systems in fabricating of three-dimensional photonic crystals for optical spectral range [15 – 17]. 20 nm thick gold films were developed on a colloidal crystal surface by means of a conventional vacuum deposition. A schematic of the structure proposed and a surface image obtained with a scanning electron microscope are presented in Figs.1, 2. Macroscopically the colloidal structures investigated are polycrystals with total volume in the range of 1 to 100 mm^3 with single crystal blocks from a few to tens microns.

Fig.2. Transmission electron microscopy image of a colloidal crystal coated with 20 nm Au film. The globule size is about 200 nm

Original surface of a colloidal crystal exhibit diffuse reflectance similar to that established for α-quartz (Fig.3). Because of macroscopic disorder inherent in the structures over sample surface and volume, coherent effects of light propagation were not pronounced when relatively large samples (10 mm^3) of colloidal crystals were examined. Colloidal crystal surface coated with a thin gold film exhibits pronounced enhancement of reflectivity with reflection coefficient monotonously increasing with wavelength (Fig.3). This behavior is characteristic for thin metal films.

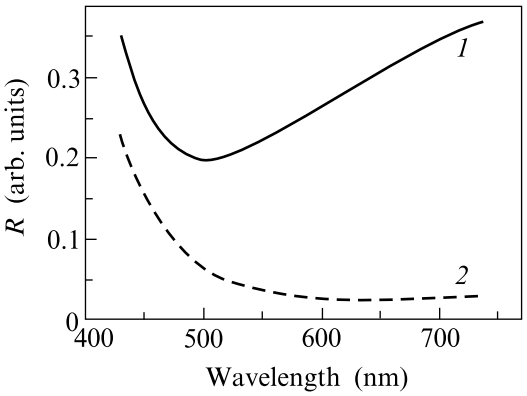

Fig.3

To test SERS efficiency of the substrates developed, mitoxantrone molecules were used deposited from an aqueous (10^{-6} M) solution on the surface of gold coated colloidal crystals. Mitoxantrone is a DNA intercalator and an anticancer drug currently used in clinical trials of non-Hodgkin's lymphomas, acute myeloid leukemia, and advanced breast cancer [18]. It is a promising complex for single molecule detection in cell organelles [19]. Earlier mitoxantrone probes were used to show that the same gold film if properly processed can be used both for Raman scattering and fluorescence enhancement [20].

Measurements performed with a cw-laser excitation (wavelength 633 nm, excitation power density about 10 mW/cm^2) showed the metal coated surface of a colloidal crystal provide an extreme Raman scattering enhancement (Fig.4). Raman signal intensity is at least 5 times higher for molecules adsorbed at colloidal crystal surface as compared to molecules at the reference metal island film deposited under the similar conditions on a plane glass plate. Note that Raman scattering signal by mitoxantrone deposited on a dielectric surface with the same excitation/registration setup is not detectable at all. The true local enhancement factor of Raman scattering by molecules adsorbed at colloidal crystal surface is significantly higher than that observed in the experiments under condition of data acquisition from a relatively large (as compared to the globule size) surface

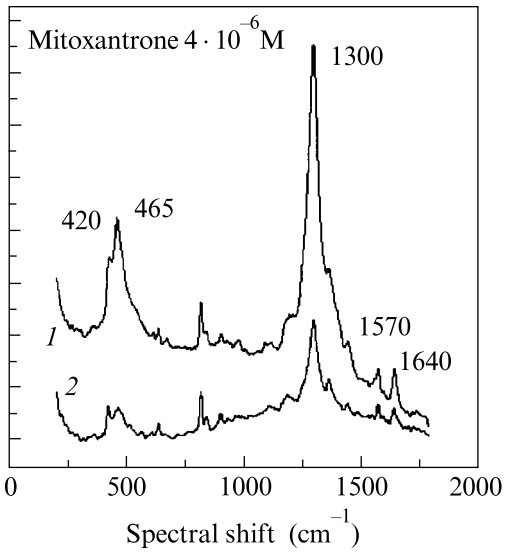

Fig.4

area. Because of colloidal crystal porosity, surface concentration of test molecules is lower than in the case of deposition on a flat surface.

Controllable lattice period provided by means of the original sol precipitation made it possible to examine size-selective features of the SERS effect. In accordance with the previously reported observations [13] we found the size selective enhancement with respect to a given laser wavelength does occur. For laser wavelength 633 nm Raman signal was found to decrease by more than one order of the magnitude when the globule diameter increased from 250 to 500 nm.

Diffuse scattering at the long wave side of the Rayleigh component in the structures investigated results from multiple incoherent scattering in a complex colloidal structure. It can be diminished when using small number of colloidal layers (down to a single monolayer) or impregnating of a colloidal crystal with immersing gel [21]. Optimization of excitation conditions (increase of excitation wavelengths up to 700–800 nm or decrease of globule size down to 150–180 nm) can increase SERS intensity considerably. With constant globule size SERS efficiency can be increased for laser wavelengths in the visible if silver films will be used instead of gold ones. This will happen because of the better overlap of the laser wavelength with plasmon resonance.

In conclusion, the first observation is reported of strong Raman scattering enhancement of molecules adsorbed at metalized colloidal crystal surface. Well-defined physical and geometrical characteristics of the structures proposed along with their good reproducibility and high durability will make possible to perform systematic studies of Raman scattering enhancement due to excitation of surface plasmons and its application in single molecule detection. As compared to the recently reported three-dimensional metal structures fabricated by means of colloidal templating [22] the metal coated colloidal crystals considered in this letter provide adsorption of the probe molecules directly at the surface which increase sensitivity of the method and is of vital importance in single molecule detection.

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