Raman Scattering Enhancement using Crystallographic Surface of a Colloidal Crystal¹

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Deposition of coinage metals on a crystallographic surface of a colloidal crystal is proposed with the aim of fabricating metal surfaces with a regular relief on a scale of 200–300 nm to get strong surface-enhanced Raman scattering (SERS). The approach is implemented through thin gold-film deposition on a surface of a crystal consisting of silica globules. Mitoxantrone molecules, a DNA intercalator, were 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-molecule detection. © 2001 MAIK "Nauka/Interperiodica".

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Strong enhancement of Raman scattering of light by molecules adsorbed at surfaces of coinage metals (Au, Pt, Ag, Ni) with a complicated nanorelief, as compared to solutions and flat dielectric surfaces (so-called surface-enhanced Raman scattering, SERS), has been extensively investigated over 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 stimulated further experimental studies of interaction of electromagnetic field with metal colloidal [6], fractal [7], and 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 the absence of reliable techniques allowing 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 nanorelief and complicate topology are used in SERS experiments. Each of these SERS-active structures features spatial inhomogeneities which are hard to describe mathematically and reproduce experimentally. Because

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of the uniqueness of each 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 the understanding of underlying physical processes and 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 10⁶-fold enhancement occurs due to excitation of surface plasmons [11, 12]. Resonant enhancement of Raman scattering was reported at a specific laser wavelength for a given metal particle size [13]. Therefore, for the 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 complicated, expensive, and includes specific processes which cannot be reduced to chemical processing.

In this letter, we propose to fabricate SERS-active periodic metal-dielectric two-dimensional nanostructures by means of metal deposition on a crystallographic surface of a colloidal crystal and report the first



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



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



Fig. 3. Reflection spectrum of the colloidal crystal surface (1) with and (2) without a thin gold film deposited thereon.

observation of pronounced Raman scattering enhancement at a colloidal crystal surface.

In the experiments, colloidal silica crystals were developed by means of centrifugation of monodisperse silica sol with the mean particle diameter varying in the range 200–500 nm. Similar structures fabricated by means of sedimentation were used earlier as model systems in fabricating three-dimensional photonic crystals for the optical spectral range [15–17]. Gold films 20 nm thick were developed on a colloidal crystal surface by means of a conventional vacuum deposition. A scheme of the structure proposed and a surface image obtained with a scanning electron microscope are presented in Figs. 1 and 2. Macroscopically, the colloidal structures investigated are polycrystals with total volume in the range of 1 to 100 mm³ with single crystal blocks from a few to tens of microns.

The original surface of a colloidal crystal exhibits 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 mm³) of colloidal crystals were examined. A colloidal crystal surface coated with a thin gold film exhibits pronounced enhancement of reflectivity, with the reflection coefficient monotonically increasing with wavelength (Fig. 3). This behavior is characteristic of thin metal films.

To test SERS efficiency of the substrates developed, mitoxantrone molecules were 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 for fluorescence enhancement [20].

Measurements performed with a cw laser excitation (wavelength 633 nm, excitation power density about 10 mW/cm^2) showed that the metal-coated surface of a colloidal crystal provided an extreme Raman scattering enhancement (Fig. 4). Raman signal intensity is at least 5 times higher for molecules adsorbed at the colloidal crystal surface, as compared to molecules at the reference metal island film deposited under similar conditions on a plane glass plate. Note that the Raman signal for 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 the colloidal crystal surface is significantly larger than that observed in the experiments under condition of data acquisition from a relatively large (as compared to the globule size) surface area. Because of colloidal crystal porosity, the sur-

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Fig. 4. Raman scattering spectra by mitoxantrone molecules adsorbed at a 20-nm thick gold film deposited (1) on a colloidal crystal and (2) on a reference glass plate.

face concentration of test molecules is lower than in the case of deposition on a flat surface.

A 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 that the size-selective enhancement with respect to a given laser wavelength occurs. For a laser wavelength of 633 nm, the Raman signal was found to decrease by more than one order of magnitude when the globule diameter increased from 250 to 500 nm.

Diffuse scattering at the long-wavelength 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 a small number of colloidal layers (down to a single monolayer) or impregnating a colloidal crystal with immersing gel [21]. Optimization of excitation conditions (increase in excitation wavelengths to 700–800 nm or decrease in globule size to 150–180 nm) can increase SERS intensity considerably. With constant globule size, SERS efficiency can be increased for laser wavelengths in the visible region if silver films are 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 of strong Raman scattering enhancement of molecules adsorbed at a metallized colloidal crystal surface is reported. Welldefined physical and geometrical characteristics of the structures proposed, along with their good reproducibility and high durability, will make it 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 increases sensitivity of the method and is of vital importance in single-molecule detection.

REFERENCES

- Surface Enhanced Raman Scattering, Ed. by R. K. Chang and T. E. Furtak (Plenum, New York, 1982; Mir, Moscow, 1984).
- I. Nabiev, R. G. Efremov, and G. D. Chumanov, Usp. Fiz. Nauk **154**, 459 (1988) [Sov. Phys. Usp. **31**, 241 (1988)].
- 3. Z. Q. Tian, Int. J. Vibr. Spectrosc. **4**, 2 (2000) (www.ijvs.com).
- 4. S. Nie and S. R. Emory, Science 275, 1102 (1997).
- 5. K. Kneipp, Y. Wang, H. Kneipp, *et al.*, Phys. Rev. Lett. **78**, 1667 (1997).
- A. M. Michaels, M. Nirmal, and L. E. Brus, J. Am. Chem. Soc. 121, 9932 (1999).
- W. Kim, V. P. Safonov, V. M. Shalaev, and R. L. Armstrong, Phys. Rev. Lett. 82, 4811 (1999).
- S. Linden, J. Kuhl, and H. Giessen, Phys. Rev. Lett. 86, 4688 (2001).
- S. J. Oldenburg, S. L. Westcott, R. D. Averitt, and N. J. Halas, J. Chem. Phys. **111**, 4729 (1999).
- A. Feofanov, E. Ianoul, E. Kryukov, *et al.*, Anal. Chem. 69, 3731 (1997).
- F. J. Garacia-Vidal and J. B. Pendry, Prog. Surf. Sci. 50, 55 (1995).
- 12. M. Xu and M. J. Dignam, J. Chem. Phys. 100, 197 (1994).
- J. T. Krug, G. D. Wang, S. R. Emory, and S. Nie, J. Am. Chem. Soc. **121**, 9208 (1999).
- M. Kahl, E. Voges, S. Kostrewa, *et al.*, Sens. Actuators B 51, 285 (1998).
- V. N. Bogomolov, S. V. Gaponenko, I. N. Germanenko, *et al.*, Phys. Rev. E **55**, 7619 (1997).
- E. P. Petrov, V. N. Bogomolov, I. I. Kalosha, and S. V. Gaponenko, Phys. Rev. Lett. 81, 77 (1998); 83, 5402 (1999).
- S. V. Gaponenko, A. M. Kapitonov, V. N. Bogomolov, et al., Pis'ma Zh. Éksp. Teor. Fiz. 68, 131 (1998) [JETP Lett. 68, 142 (1998)].
- T. D. Shenkenberg and D. D. von Hoff, Ann. Intern. Med. 105, 67 (1986).
- A. Feofanov, S. Sharonov, I. Kudelina, *et al.*, Biophys. J. 73, 3317 (1997).
- N. Strekal, A. Maskevich, S. Maskevich, *et al.*, Biopolymers 57, 325 (2000).
- 21. M. Kapitonov, N. V. Gaponenko, V. N. Bogomolov, et al., Phys. Status Solidi A 165, 119 (1998).
- 22. M. Tessier, O. D. Velev, A. T. Kalambur, *et al.*, J. Am. Chem. Soc. **122**, 9554 (2000).