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Hydrophobic ZnO-Based Substrates with Nanostructures of Gold and Silver for SERS Spectroscopy of Standard Organic Dye

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In this study, hydrophobic ZnO-based substrates covered with nanostructures of gold and silver are proposed as surface enhanced Raman scattering (SERS) active substrates for identifying the spectra of rhodamine 6G molecules using a portable spectrometer by Thermo Fisher Scientific. It is demonstrated that the use of a hydrophobic substrate contributes to the concentration of the investigated substance molecules at a focal point during solvent evaporation. Concentrating the molecules allows for measuring SERS spectra using compact spectrometers with a focusing area in the order of hundreds of microns. The mechanism enhancing the sensitivity of the SERS spectroscopy method is discussed, which is based on the formation of 'hot' spots on the hydrophobic surface with developed relief, modified by noble metals.

Keywords: SERS, hydrophobicity, zinc oxide, silver, gold, rhodamine 6G.

Surface-enhanced Raman scattering (SERS) spectroscopy is a promising technique for identification of molecular footprints of substances. It relies on the nonlinear effect of Raman scattering (RS) of light wherein a photon absorbed by a molecule gets scattered with a shift in energy. High sensitivity, resolution [1], and signal stability [2] and the potential for examination of ultralow concentrations of substances with the use of substrates with nanostructures [3] are the advantages of SERS spectroscopy. In addition, it is a nondestructive method that allows one to analyze an object without damaging it. This is useful, e.g., in biological studies [4]). The key mechanism of RS signal amplification is the electrodynamic one. This amplification is supported by the so-called „hot" spots localized in nanometer gaps and at irregularities of plasmonic nanoparticles [5].

The development of hydrophobic SERS substrates is a promising option for express detection of RS spectra at ultralow concentrations of organic molecules. In contrast to hydrophilic substrates, hydrophobic ones prevent the spreading of matter over the surface (preliminary concentration method), thus making it possible to combine electrodynamic and chemical signal amplification effects and reveal a finer structure of SERS spectra at low substance concentrations [6]. The greater the contact angle is, the higher is the intensity of the detected SERS signal. For example, one may use electron-beam lithography both to reproduce natural hydrophobic coatings [7] and fabricate a SERS-active substrate based on a periodic lattice of gold nanoantennas [8]. However, owing to the costliness and complexity of the process, this method is ill-suited for industrial application and express testing. A method for fabrication of hydrophobic ZnO-based coatings is known [9,10].

Under certain ZnO growth conditions, an ensemble of hexagonal needle-shaped crystals, which support the „lotus effect," may be formed. The modification of such structures with plasmonic nanoparticles opens up the possibilities for enhancing the sensitivity of SERS spectroscopy [11]. Owing to the simplicity of synthesis, these substrates hold much promise for use in express identification of substances in the field of detection of hazardous and prohibited compounds [12] and have various other potential practical applications (e.g., in the food industry [13]). Silver nanoparticles are better suited for the purpose than gold ones: not only are they cheaper to produce, but sufficiently small silver nanoclusters also provide very strong optical absorption and emission [14]. It should be noted that the signal on these SERS substrates modified with silver nanoparticles is stabilized by the processes of electron transfer between zinc oxide and silver of an oxidation-preventing surface [15]. ZnO may be modified with silver either by thermal evaporation [16] or by adsorption of a colloidal solution [17]. Since it is hard to control uniformity in the course of adsorption deposition, the signal stability remains low in such systems. A more uniform coating may be synthesized by thermal evaporation of silver.

In the present study, SERS-active substrates based on hydrophobic ZnO structures with a silver coating designed for express characterization of Raman scattering spectra are examined. Molecules of a standard organic dye (rhodamine 6G, R6G) dissolved in water in a concentration of 10^{-5} M are used as an example of a compound to be identified. The results are compared to those obtained for similar ZnO structures coated with gold.

Hydrophobic ZnO structures (type I) synthesized on sapphire substrates by catalytic gas-phase synthesis were used as SERS-active substrates. The gas phase consisted of zinc vapor and an argon–oxygen mixture (with 10% of oxygen). The growth reactor was evacuated in advance to a residual pressure of 10 Pa. The synthesis conditions were as follows: the evaporation zone temperature was 630°C, and the growth zone temperature was 580°C. The synthesis time was 20 min. Pointed ZnO structures were formed on the substrate by reducing dramatically the temperature in the zinc evaporation zone.

ZnO structures were coated with metallic layers of silver (type II) and gold (type III) by thermal evaporation with the use of a „SAHA" vacuum coater (Dana Inzhiniring, Moscow). Simultaneous deposition onto smooth substrates under the same conditions was performed to estimate the thickness of deposited layers. The thickness of silver and gold layers was ~ 200 and 170 nm, respectively. Microscopic studies were carried out with a JEOL JSM-7401 scanning electron microscope.

The contact angle was determined by analyzing video images of a sessile droplet. The examined ZnO surface was positioned strictly horizontally between a camera and a diffuse light source. Droplets of a 10^{-5} M aqueous solution of R6G $3\,\mu l$ in volume were deposited with a pipette onto all samples. A MATLAB code was used to record a 3-min-long video of a droplet and analyze it in order to determine the contact angle.

SERS spectra were recorded with a portable spectrometer (produced by Thermo Fisher Scientific) and a laboratory Horiba LabRAM HR Evolution spectrometer. The SERS spectra measurement procedure was as follows: a droplet of a 10^{-5} M solution of organic dye R6G $3\,\mu l$ in volume was deposited onto a sample and dried for $5-10$ min in air. The excitation radiation wavelength was 785 nm in both spectrometers. In the portable spectrometer, the exposure time was 2 s and 15 min for samples type II (with silver) and type III (with gold), respectively. In the laboratory spectrometer, the measurement time of SERS spectra of R6G was 2 s for samples type II and III, and the RS spectrum of R6G molecules on pure ZnO (sample type I) was recorded within 10 s. The diameter of R6G droplets on the surface of zinc oxide with silver and gold coatings was $837\,\mu m$ and $1214\,\mu m$, respectively. Spectrometers differed in the exposure area: the laser spot diameter was several hundred micrometers for the portable spectrometer and $1\,\mu m$ for the laboratory spectrometer. The laser power in measurements of spectra with the portable and laboratory spectrometers was 260 and 150 mW, respectively.

According to the electron microscopy data, a ZnO deposit (type I) of a complex morphology formed in the process of catalytic gas-phase synthesis on sapphire substrates. Both pointed structures up to $200\,\mu m$ in length and platelets $5-10\,\mu m$ in thickness were observed. Zinc oxide grows rapidly along the [001] crystallographic direction, forming these pointed structures and platelets. Contact angle θ

for the type I sample was on the order of 150°, which corresponds to a nearly superhydrophobic state.

At the next stage, silver (ZnO/Ag, type II) and gold (ZnO/Au, type III) was deposited onto the surface of the type I sample. The deposited layers differed in micromorphology (see Figs. 1, a and b). Gold forms an island structure with individual elements having lateral dimensions as large as several tens of micrometers, while the silver coating is more uniform. Since gold and silver were deposited onto a „cold" surface of the type I sample with the diffusion activity of adatoms being at a minimum, the adhesion of metals to the surface of zinc oxide plays a major role. Silver is distinguished by its good adhesion, forming a continuous film. Owing to its weak adhesion, deposited gold breaks up into islands as the layer thickness increases. Topographic irregularities (active elements of the ZnO surface structure) may also have a major effect on the process. Contact angle θ decreases to 141.5° and 136.5° after the deposition of silver (type II) and gold (type III). This is apparently attributable to the specifics of interaction between R6G molecules and noble metals. Since the concentration of dye molecules after evaporation of the deposited solution is correlated with the contact angle, samples type I and III feature the highest and lowest concentrations, respectively.

A dense and uniform plasmonic modifying layer is needed primarily for stabilization of the SERS signal and to ensure its reproducibility in spectra throughout the entire substrate surface. If these two conditions are sufficiently satisfied, it becomes possible to use such surfaces as SERS substrates for express identification of substances with portable spectrometers. It should be noted that the measured SERS spectrum is the result of averaging of signals of all molecules within the laser irradiation spot [18]. Thus, the uniformity of a modifying coating has an effect on the suppression of spectral noise, which reduces artificially the signal intensity via averaging performed in the course of spectrum recording.

Figure 2, a shows the RS and SERS spectra of R6G adsorbed on samples type I, II, and III. These spectra were recorded with the laboratory spectrometer. The peaks of R6G molecules are finely resolved in the spectra of samples type II and III coated with noble metals. Since the type I sample had the highest dye concentration after droplet evaporation and a low-intensity RS spectrum (after baseline subtraction), one may note that the effect of plasmonic amplification at noble metal particles was instrumental in shaping the RS spectrum. The most intense (with a 5-fold amplification) spectrum was obtained for the type II sample coated with silver. This is attributable to a high RS cross section, which is associated with a high absorption capacity of silver. Similar results were obtained in measurements with the portable spectrometer (Fig. 2, b). Key material peaks consistent with literature data [19,20] are present in the SERS spectra of R6G (Fig. 2, b) adsorbed on ZnO surfaces coated with both gold and silver. Vibrational modes of the C−C aromatic ring
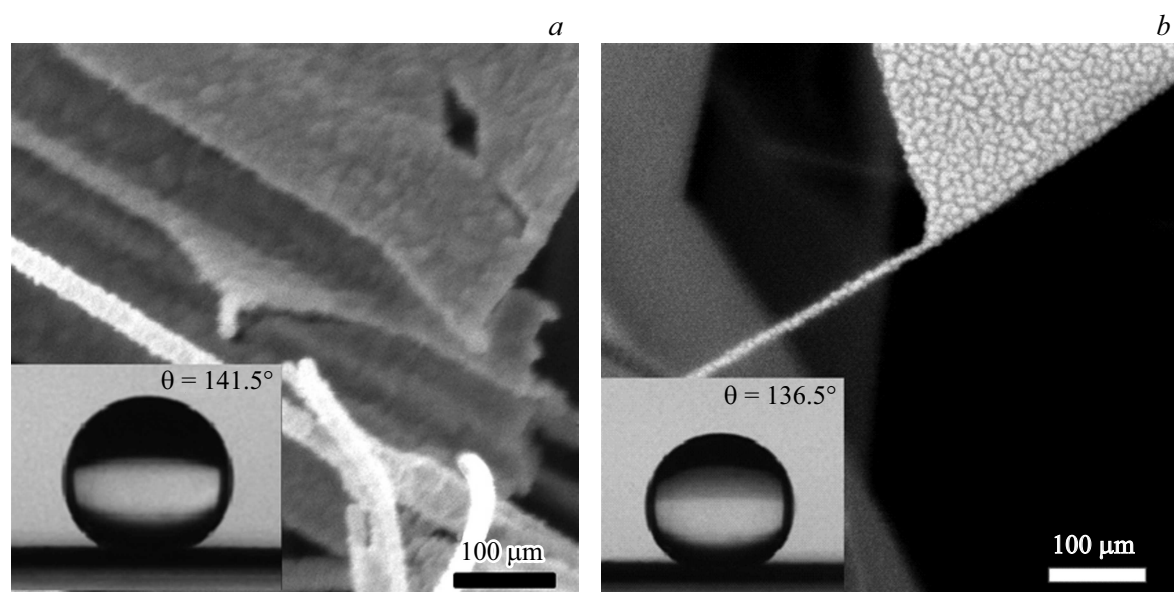
Figure 1. Microscopic images of the surface of hydrophobic samples type II (*a*) and III (*b*). The corresponding contact angles are shown in the insets. A droplet of organic dye R6G 3 μl in volume was deposited.
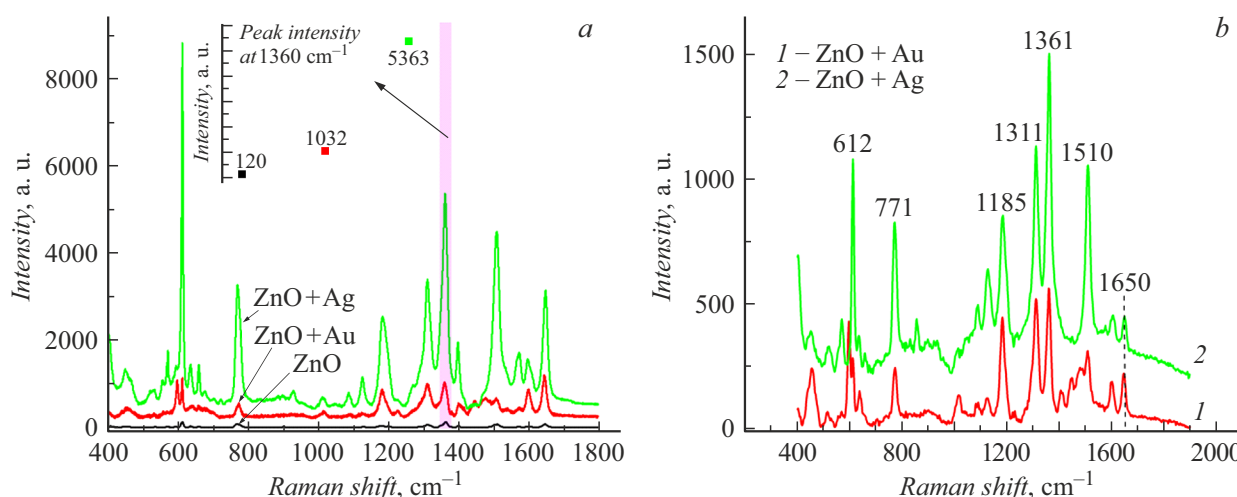

Figure 2. RS and SERS spectra of samples type I, II, and III measured with a Horiba LabRAM HR Evolution laboratory spectrometer (*a*) and samples type II and III measured with a Thermo Fisher Scientific portable spectrometer (*b*).

(1650, 1510, 1361 cm^{-1}), C−O−C (1311 cm^{-1}), C−H (771 cm^{-1}), and ring C−C−C (612 cm^{-1}) are seen clearly in the spectra. Although the intensity of R6G spectra on the ZnO/Ag surface was higher, the ZnO/Au sample provides a more detailed spectrum and a finer resolution of peaks. Note that the fluorescence background was not detected after modification with silver and gold. This contributed to an increase in the signal quality. In addition, since the coating was hydrophobic, a deposited R6G droplet did not spread over the substrate surface, thus increasing the number of molecules in the spectrum measurement region. The choice of a specific metal is dictated by the research objective and the wavelength of excitation radiation used in the experiment. Figure 3 presents the comparison of SERS spectra of R6G on the surface of the type II sample measured with the portable and laboratory spectrometers. It can be seen that the intensity of individual spectral lines recorded with the laboratory spectrometer, which provides point focusing, increases by no more than 30% compared to the spectrum intensity obtained using the portable spectrometer. this insignificant difference suggests that a highly developed surface complicates the process of focusing. A large exposure area in experiments with the portable spectrometer is an advantage, since it raises the probability of detection of molecules localized directly at the tips of pointed ZnO structures coated with gold and silver nanostructures. Integrated RS and SERS spectra are obtained in the process of measurements, and the signal
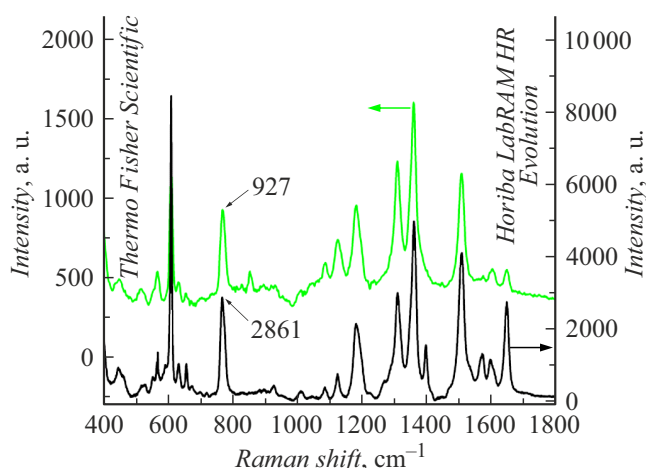
Figure 3. SERS spectra of type II samples measured with the portable and laboratory spectrometers.

intensity increases with increasing number of „hot" spots in the exposure area.

Thus, SERS-active substrates based on hydrophobic ZnO coated with gold and silver nanostructures were proposed to be used for express identification of Raman scattering spectra of rhodamine 6G molecules with a portable Thermo Fisher Scientific spectrometer in the field. It was demonstrated that the hydrophobic properties of the surface of SERS-active substrates combined with resonance effects at metallic structures provide an opportunity to enhance the intensity of RS spectra (due to an increased concentration of molecules in the scanning region). Owing to a high absorption capacity of silver, express identification on SERS-active ZnO/Ag substrates with a high intensity of spectral lines is achieved within 2 s of measurement at an R6G dye concentration of 10^{-5} M. At the same time, ZnO/Au substrates provide more detailed spectra with less noise. The simplicity of synthesis and high resolution attainable in express identification of substances make the proposed SERS-active substrates well-suited for application in the field of security and other practical applications.

Conflict of interest

The authors declare that they have no conflict of interest.

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