Development of self-cleaning SERS-active nanostructures based on ZnO nanorods and Ag nanoparticles

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Abstract. This work demonstrates the possibility of using a combination of zinc oxide nanorods with silver nanoparticles as a self-cleaning SERS substrate. In addition to Raman scattering enhancement such structures demonstrate the self-cleaning effect during UV treatment. The ZnO nanorods (NRs) array was synthesized on a ZnO seed layer by the hydrothermal method. The Ag nanoparticles (NPs) array was formed by vacuum thermal evaporation over the ZnO NRs. Rhodamine-B 230 μM solution has been detected using the formed SERS-substrates without additional mathematical processing of the Raman spectra. Subsequent UV radiation treatment showed a 3-fold decrease in the intensity of the spectral peaks of the analyte.

1. Introduction
The effect of surface enhance Raman scattering (SERS) has been known since the 80s of the 20th century [1]. The metal nanoparticles (such as Ag, Au, Cu) due to localized surface plasmon resonance (LSPR) provide multiple enhancement of the Raman scattering from the molecules of the test substance [2-5]. SERS diagnostic allows the detection of ultra-low analyte concentrations down to individual molecules on the sensor surface.

Most often, for practical needs, planar SERS sensors are manufactured, consisting of a dielectric substrate coated with a dispersed metal film or nanoparticles. Such structures have an average enhancement factor in the region of 10⁵-10⁶. In most cases, the substrates are disposable. One way to achieve reusability is through the use of photocatalytically active layers (for example, ZnO or TiO₂) in the structure of SERS substrates in combination with metal nanoparticles. As is known, such combination allows using the LSPR effect to increase the efficiency of organic compound decomposition, which contributes to the self-cleaning of the surface from the analyte [6, 7].
In this work, three-dimensional SERS substrates were fabricated based on ZnO nanorods coated with silver nanoparticles. The Radomin-B solution (concentration 230 μM) used as an analyte. It was confirmed that the combination of ZnO nanorods and silver nanoparticles allows the analyte to be removed from the surface during UV treatment.

2. Experiment
To fabricate the structure we used silicon wafers (n-type) with 300-nm-thick SiO$_2$ layer. The substrates was pretreated in Caro’s acid solution, ammonia and hydrogen peroxide mixture solution, and followed by rinsing in deionized water. A 100-nm-thick ZnO seed layer was formed by the magnetron sputtering method. The synthesis of ZnO nanorods was carried out by the hydrothermal method (figure 1). The synthesis solution consisted of urotropine (C$_{6}$H$_{12}$N$_{4}$; CAS number: 1015846-51-1), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O; CAS number: 10196-18-6) and deionized water in the proportion 14:3:200. The synthesis of ZnO NRs was carried out at a temperature of 80 °C, for 30 minutes, with constant stirring of the solution. Then the substrates were washed in a stream of deionized water and dried in argon atmosphere.

![Figure 1. Schematic representation of an experimental setup for the synthesis of ZnO NRs: 1 - tripod; 2 - stirrer rotation source; 3 - working solution; 4 - holding foot; 5 - substrate holder; 6 - capacity for a water bath; 7 - silicon substrate with a seed layer; 8 – stirrer.](image)

The formation of silver nanoparticles over ZnO NRs array was carried out in two stages. At the first stage, silver deposited onto the substrate by thermal vacuum deposition. The weight portion of silver was 6 mg. The residual pressure in the chamber was $3 \times 10^{-5}$ Torr. The distance between the molybdenum evaporator and the substrate was 20 cm. The second stage was annealing in the atmosphere at a temperature of 400 °C for 10 minutes.

The morphology of the structures was studied using a Thermo Scientific ™ Quattro SEM scanning electron microscope with parameter, showed in figure 3 and figure 5.

The 4 μL drops of 230 μM RB solution were put on fabricated SERS-substrates. Then the analyte dried in atmosphere at room temperature. The samples studied on a LabRAM HR Evolution (Horiba) Raman spectrometer at laser wavelength of 514 nm, power of 0.5 μW, and ×100 focal lens at room temperature. Laser radiation focused on a sample surface with an area of 20 μm$^2$. The spectrum recorded within 50 s. The general scheme for the manufacture and application of SERS structures show in figure 2.
The study of the photocatalytic activity of the structures was carried out by treatment with a UV light-emitting diode followed by the study of the analyte intensities on a Raman spectrometer. The maximum radiation of the diode occurs at a wavelength of 405 nm, a luminous flux density of 94 mW/cm². The distance between the LED and the substrate was 10 cm; the irradiation time was 120 minutes.

Figure 2. Scheme of the fabrication and application of the ZnO NRs / Ag NPs combined SERS-substrate.

3. Results and discussion
Figure 3 shows a SEM image of ZnO nanorods array synthesized on a silicon substrate. The histograms of distribution of the thickness and length of ZnO NRs are demonstrated in figure 4a and 4b. As it can be seen, the layer of nanorods turned out to be rather uniform. The prevailing thickness and length of nanorods are 36 and 220 nm, respectively. The distance between adjacent ZnO nanorods varies from 2 to 60 nm.

Figure 3. SEM images of the ZnO NRs array.
Figure 4. Histograms of distribution of thickness (a) and length (b) ZnO NRs on an area of 1 μm².

Ag nanoparticles formed by vacuum thermal evaporation and atmospheric annealing have covered a significant surface area of ZnO nanorods (figure 5a). It should be noted that the average sizes of NPs on the walls and tops of the nanorods differ and amount to approximately 7 and 20 nm, respectively (figure 5b, 5c).

Figure 5. SEM images of the surface of the ZnO NRs / Ag NPs structure (a), histograms of the size distribution of Ag NPs on the walls (b) and vertices (c) of ZnO NRs.

As shown by the results of Raman spectroscopy, the obtained SERS structures allow the detection of the main spectral lines of rhodamine-B at 230 μM concentration. Figure 6 shows the Raman spectra of the analyte obtained using the initial ZnO NRs array and the array of ZnO NRs decorated with Ag nanoparticles. The structure of ZnO NRs with Ag NPs provides 5 times more enhancement than structures of ZnO NRs without nanoparticles. According to [8] the enhancement factor obtained by...
comparing the intensities of the peak at 1650 cm\(^{-1}\) of rhodamine-B on glass and ZnO NRs/Ag NPs structure was 10\(^3\). It should be noted that the applied concentration of rhodamine-B is not the sensitivity limit of our SERS-substrate and was chosen to demonstrate the possibility of self-cleaning of the fabricated SERS structures.

The study of the self-cleaning ability of the fabricated SERS substrates showed that structures with and without particles exhibit different activity of analyte decomposition under UV irradiation. The spectral band \(\sim 1650\) cm\(^{-1}\) (C–C\(_x\) stretch) confirmed by several researchers as one of the most characteristic bands for RB [9-11], chosen as a standard. UV treatment of the ZnO NRs structure reduced the intensity of the rhodamine-B spectral lines by 1.12 times, while the ZnO NRs / Ag NPs structure shows a decrease in intensity by more than 3 times (figure 7). This result indicates that plasmonic metal nanoparticles enhance the photocatalytic decomposition of organic substances by ZnO nanostructures.

**Figure 6.** Comparison of 230 \(\mu\)M RB Raman spectra on the ZnO NRs and ZnO NRs / Ag NPs structures before and after UV treatment.

**Figure 7.** Comparison of the intensity of the 1650 cm\(^{-1}\) peak on the ZnO NRs and ZnO NRs / Ag NPs structures before and after UV treatment.
4. Conclusion
The three-dimensional SERS-substrates fabricated in this work based on ZnO nanorods allow the detection of 230 μM Rhodamine-B solution concentration. The structures of ZnO NRs decorated with Ag NPs show the $10^3$ enhance factor and threefold decrease in the rhodamine-B spectral line intensity after UV treatment. Thus, the possibility of organic matter enhance decomposition by SERS-structures with metallic NPs under the UV radiation demonstrated. This approach suggests the possibility of using a ZnO NRs / Ag NPs combination for the fabrication of self-cleaning SERS structures.

Acknowledgement
This work was supported by the State assignment 2020-2022 № FSMR-2020-0018

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