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Pesticides detection by SERS using dendritic structures grown in glass

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Abstract. We demonstrate that dendritic structures formed in glass by electrolysis of silver ions-enriched glass allow detection of low concentration of pesticide thiram using surface- enhanced Raman scattering spectroscopy. Thiram detection is an important issue due to its toxicity for humans. Silver ions were embedded in glass using $Ag^+ \leftrightarrow Na^+$ ion exchange procedure. Electrolysis was performed at 250 °C under 600 V and resulted in formation of silver dendrites under the glass surface. To remove the surface glass layer and ensure the access of pesticide to the dendritic structures for Raman spectroscopy we etched the glass in low-concentrated HF solution. Pesticide was adsorbed on the surface of the dendrites via drying a droplet of its aqueous solution. The detection limit and Raman enhancement were estimated, being $4.6 \cdot 10^{-10}$ g/mm² (about a monolayer) and ~ $4 \cdot 10^5$, respectively. The influence of the morphology of the dendritic structures on Raman signal distribution and enhancement were also studied.

Keywords: surface enhanced Raman scattering spectroscopy, dendrites, electrolysis

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Дендритные структуры для обнаружения пестицидов методом гигантского комбинационного рассеяния

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Аннотация. Мы продемонстрировали, что металлические дендритные структуры, сформированные методом электролиза в обогащенном ионами серебра стекле, позволяют детектировать малые концентрации пестицида тиурама методом гигантского комбинационного рассеяния. В рамках работы были установлены предел обнаружения пестицида и коэффициент усиления комбинационного рассеяния дендритами, а также изучено влияние морфологии дендритов на пространственное распределение сигнала гигантского комбинационного рассеяния.

Ключевые слова: гигантское комбинационное рассеяние, дендриты, электролиз

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Introduction

Raman scattering is an inelastic scattering of light by vibrational modes of a molecule [1]. The frequency of scattered light depends on a vibration mode and, since sets of modes are unique for each specific molecule, one can identify various species using their Raman spectra. Since one of a million photons is involved in this type of inelastic scattering, Raman spectroscopy cannot detect low concentration of molecules. Surface-enhanced Raman spectroscopy (SERS) allows the essential increase in detection limit of the Raman scattering by using metal nanostructures. Metal nanostructures enhance scattering efficiency [2], which allows ultra-sensitive detection and identification of low concentration of molecules [3]. The applicability of metallic nanoparticles [4], dendrites [5] and nano-island films [6] in SERS has been demonstrated. Using dendrites in SERS is very promising due to numerous "hot spots" (areas of electric field maximum) at the edges and tips of the trunk and branches of the dendrites [7].

One of the important SERS applications is monitoring pesticides in food [8], since pesticides are widely used in modern agriculture [9]. In comparison with the classical methods of pesticide detection, such as gas chromatography, mass spectrometry, and high-performance liquid chromatography, SERS offers faster detection time, simpler sample preparation, portability and reduced cost [10]. Substrates with dendritic structures on the surface can be applied in SERS for the detection of low concentration of pesticide, down to 10^{-10} M [11]. For example, one can use SERS for the detection of thiram ($C_6H_{12}N_2S_4$), which is sulfur fungicide widely used in agriculture [12, 13]. Thiram is toxic for humans when both consumed and in contact with the skin, and effective techniques for its detection in food are highly needed [14]. In this paper, we present the approach to the detection of low concentration of thiram by SERS using dendritic structures on the glass surface.

Materials and Methods

Silver dendritic structures were formed by the electrolysis of a silver-enriched glass followed by chemical etching [15]. We used $Ag^+ \leftrightarrow Na^+$ ion exchange to introduce silver ions in soda-lime glass slide "Menzel": the slide was immersed in the melt of 5 wt.% AgNO₃ and 95 wt.% NaNO₃ for 20 min at the temperature of 325 °C. Then we deposited aluminum electrodes (thickness of 200 nm) on the opposite sides of the glass slide and applied DC voltage (600V) to the glass at the elevated temperature (250 °C). Dendritic structures were formed via the reduction of silver ions by electrons and clustering of silver atoms near the cathode surface of the slide. The passed charge during the electrolysis was 1.1 C. After the electrolysis, we immersed the slide in the etchant (5 g NH₄F:40 g H₂O:5 µl HF) for 10 min to remove the surface glass layer and ensure the access of pesticide to the dendritic structures for SERS experiments. The passed charge and the duration of the etching were chosen to provide maximum of Raman enhancement [15].

Dendritic structures were characterized using the atomic-force microscope (AFM, Veeco Dimension 3100, Bruker). The images were analyzed using Gwyddion software [16].

Dendritic structures were tested as a SERS-active substrate for pesticide thiram detection. SERS measurements were performed using the confocal Raman microscope (LabRAM HR800, Horiba, Japan) with 100x objective and 784.19 nm excitation laser. Laser wavelength was chosen to avoid photoluminescence of thiram. We deposited 2 μ l droplets of 1·10⁻⁴ M aqueous solution of thiram on the surface of the pristine glass slide and the slide with formed dendritic structures, and let droplets dry in air at room temperature. Note, the drying of the droplet on the surface of the pristine glass resulted in the crystallization of thiram. To measure the size of the formed crystals we used the optical profilometer (NewView 6000, Zygo, Middlefield, CT, USA). We also

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tested lower concentrations of thiram in SERS. The $1 \cdot 10^{-4}$ M solution of thiram was subsequently diluted with water to reach $1 \cdot 10^{-6}$ and $1 \cdot 10^{-8}$ M concentrations, 2 µl droplets of these solutions were deposited and dried on the surface of the dendrites. SERS (from thiram on dendrites) and Raman (on glass) spectra were collected for 2 and 20 s, respectively, in the spectral range of 230–1560 cm⁻¹. The laser power was the same for SERS and Raman measurements. The SERS spectra were measured in 100 points over the area of 5×5 µm².

Results and Discussion

In figure 1 we present optical and 3D AFM images of the formed dendrite structures. One can see, the surface consists of microstructures with lateral size of several micrometers and nanostructures with size of about 100–250 nm. The average height of the nanostructures is ~ 1 μ m, while the microstructures' height is ~ 10 μ m.

Raman spectra of thiram acquired from the virgin glass slide and the slide with dendritic structures in frequency regions $500-900 \text{ cm}^{-1}$ and $1000-1560 \text{ cm}^{-1}$ are demonstrated in figures 2, *a* and *b*, respectively. One can see, the band at 1386 cm⁻¹, which is assigned to CH₃ symmetric bending, is the most intense one in the SERS spectra measured using the dendritic structures, whereas for the spectra measured from the glass slide the band around 560 cm⁻¹ is the most intense one [17].



Fig. 1. Optical (a) and AFM (b) images of the dendritic structures on the glass surface

The decrease in S-S bond (560 cm⁻¹) intensity is due to thiram interaction with the metallic surface of dendrites following the bond cleavage of thiram [18]. Therefore, a relative standard deviation (RSD) of the SERS signal and enhancement factor were evaluated using 1386 cm⁻¹ band.



Fig. 2. Raman and SERS spectra of thiram acquired from the virgin glass slide and from the slide with dendrites in different spectral range (a, b)

To study the influence of the dendrites' morphology on the enhancement of Raman signal we measured the SERS spectra in the areas containing nanostructures and microstructures covered with thiram (area of dried droplet of $1 \cdot 10^{-4}$ M aqueous solution). The results are presented in figure 3. The signal collected in the area of the microstructure (point 1) has low intensity, while the nanostructures (point 2) demonstrate a high-intense SERS signal. The signals differ tenfold.

We attribute the observed difference in the signals to the non-uniform distribution of thiram molecules. Supposedly, the most of the thiram molecules are located between the microstructures (on the nanostructures).

To calculate the surface concentration of thiram molecules on the nanostructures we evaluated the area between microstructures using the optical image of the $1\cdot10^{-4}$ M droplet dried on the dendrites' surface. The area of the droplet was 1.4 cm², the ratio of the areas occupied by microstructures and nanostructures was 0.74, the mass of thiram contained in the droplet was $4.8\cdot10^{-8}$ g.

Thus, the surface concentration of thiram on the nanostructures was about $N_{\text{SERS}} \sim 4.6 \cdot 10^{-10} \text{ g/mm}^2$, which corresponds to the monolayer of thiram. Note that drying of the same droplet on the surface of the pristine glass resulted in the crystallization of thiram. We measured the height of the crystals using optical profilometer ($h \sim 1.1 \, \mu\text{m}$) and estimated the concentration of thiram in the crystal according to $N_{\text{RS}} = \rho \cdot h = 1.6 \cdot 10^{-6} \, \text{g/mm}^2$, where ρ is thiram density (~ 1.3 g/cm³).



Fig. 3. Optical image of the dendritic structures and SERS spectra of thiram collected from the area of a microstructure (1 point) and nanostructures (point 2)

We calculated Raman enhancement factor (EF) provided by the nanostructures using the calculated concentrations:

$$EF = \frac{I_{SERS}}{I_{RS}} \cdot \frac{N_{RS}}{N_{SERS}} \cdot \frac{t_{RS}}{t_{SERS}},$$
(1)

where I_{SERS} , N_{SERS} , t_{SERS} are the integral intensity of 1386 cm⁻¹ peak (1380–1400 cm⁻¹) averaged over ~ 100 SERS spectra, thiram surface concentration and the acquisition time in SERS measurements, respectively. I_{RS} , N_{RS} , t_{RS} are the integral intensity of the same peak averaged over ~ 10 Raman spectra, the concentration of thiram in crystals and acquisition time, respectively, for Raman measurements. The ratio of integral intensities was $I_{\text{SERS}}/I_{\text{RS}} \sim 13$, the ratio of the acquisition times was $t_{\text{RS}}/t_{\text{SERS}} = 10$ and the ratio of concentrations was $N_{\text{RS}}/N_{\text{SERS}} = 3\cdot10^3$ in our measurements. Thus, the enhancement factor of the dendritic nanostructures is ~ 4\cdot10^5.

Note, we could not detect any signal in the case of the SERS measurements using droplets of 10^{-6} and 10^{-8} M aqueous solutions of thiram. These droplets were strongly spreading out across the sample during the drying, which resulted in extra low, less than a monolayer, surface concentration of thiram.

Finally, we obtained the spatial distribution of SERS signal across the sample with the dendrites. Figure 4 presents the distribution of integral intensity of the 1386 cm⁻¹ peak and the corresponding optical image. The SERS map demonstrates non-uniform SERS signal distribution which is supposedly due to the non-uniform distribution of thiram. As we discussed above, most of the thiram molecules are located between the microstructures. Therefore, RSD of the SERS signal is 99.5%.



Fig. 4. Spatial distribution of integral intensity of 1386 cm⁻¹ peak across the surface with dendrites (a) and corresponding optical image (b)

Conclusion

We demonstrated that SERS can be applied for the detection of low concentration of pesticide thiram using dendrite structures. Dendrites were fabricated by the electrolysis of the glass slide enriched with silver ions, and "opened" with subsequent chemical etching. The detection of thiram in surface concentration of $4.6 \cdot 10^{-10}$ g/mm² (a monolayer) is demonstrated. The Raman enhancement provided by the dendrites is $4 \cdot 10^5$.

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