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Development of Sensor Substrates Based on Melamine-Barbiturate-Silver Supramolecular Assemblies

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Introduction. Over the recent years, microstructured nanosized silver, gold and copper substrates have been of great interest in the field of surface-enhanced Raman spectroscopy (SERS). Accurate analysis requires a substrate that amplifies inelastic light scattering due to surface plasmons, allowing virtually error-free detection of the substance even at very low concentrations (up to a few molecules). Several types of surface-enhanced Raman substrates currently exist, such as metal nanoparticles in suspension, metal particles immobilized on solid or disposable paper substrates, and nanostructures fabricated directly on solid substrates. However, there are several problems with such platforms that need to be solved. One of them is surface degradation over time, which includes physical and chemical sorption of molecules on the surface, leading to signal degradation. Another problem is the inability to reuse substrates. Our challenge is to solve these problems. Based on the hypothesis that metal nanoparticles can be fixed on the substrate, we assume that this will ensure the reliability of the system and the prospect of its multiple use. This work will present a simple method of obtaining a substrate for surface-enhanced Raman spectroscopy, which does not require complicated syntheses and special equipment, in order to solve the previously mentioned problems in this area.

Main part. In the first step, the initial 20 mM solutions of melamine and barbituric acid were mixed and stirred in equal proportions (0.5 ml). The result was a self-assembled MBA (melamine and barbituric acid) complexes. After that, 1 ml of 20 mM AgNO3 solution was added to the resulting particles, followed by 60 μl of 10% aqueous ammonia solution to neutralize and accelerate the recrystallization process. The next step was to put a 10 μl drop to the surface of quartz glass (SiO_2). After putting the drop, a periodic hexagonal film began to form on the surface. When it was completely dry, it was calcined in a muffle furnace at different temperatures: 400°C 1 hour and 600°C 3 hours; 600°C 1 hour and 800°C 3 hours. As a result, silver micro- and nanoparticles were deposited on the surface of the quartz glass.The resulting structures were examined by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis and XRD to determine the phase of the silver particles. The result of the study showed the presence of metallic silver in the sample. Also, in this work it was necessary to use atomic force microscopy (AFM) to identify the shape of silver agglomerates and their immersion in the quartz substrate. Thus, the silver agglomerates were found to be hemispheres in shape, with an average height above the surface of the substrate of about 220 μm. After that the Voronoi entropy was calculated for the substrates obtained at different temperatures. The Voronoi entropy values for the substrates obtained at different temperatures are almost indistinguishable. Consequently, the wafers obtained by the method presented in this work represent a structure with conserved periodicity, as proved by calculating the Voronoi entropy (S = 1.32 for 400-600° and S = 1.28 for 600-800°). Two samples obtained at 400-600 and 600-800° were analyzed to compare the SERS effect. The preset settings of the Raman spectrometer were a 514 nm laser with an intensity of 1% of the initial beam and a single point exposure time of 1 s. Rhodamine 6G dye with a concentration of 10-5 M was used as the analyte. The structures obtained by firing at lower temperatures showed the best result. This effect can be explained by the fact that the SERS effect is more contributed by metal particles of smaller size due to a higher concentration of surface plasmons and a stronger electromagnetic field at the conductor-dielectric boundary.

Conclusions.

1. A supramolecular film with a hexagonal structure made from melamine-barbirurate-silver solution was made

2. The possibility of obtaining periodic silver nanoagglomerations by thermal treatment of metal-organic silver complexes has been documented

3. Studies by SEM, EDX, XRD and AFM methods have been performed

4. Structural regularity data were obtained using Voronoi entropy with MATLAB and ImageJ software packages

5. As a result of the study, samples of quartz substrates containing agglomerations of silver particles were obtained, which can be applied in surface-enhanced Raman spectroscopy (SERS).

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