# Supporting Information

## Silver melamine thin film as a flexible platform for SERS analysis

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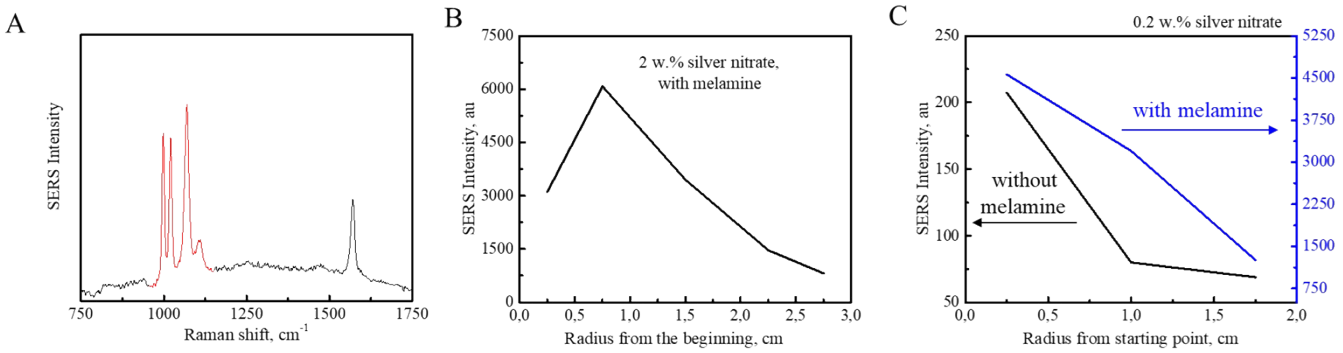


Figure 1. A. SERS spectrum of benzene thiol, absorbed by silver particles in agar gel. Reference peak is highlighted. B. Comparison of SERS intensity of benzene thiol on silver gradient structure with and without melamine. C. Regularity of intensity changing for structure formed with 2 w.% silver nitrate.

The structured films were investigated via Raman spectroscopy. Benzene-thiol is used as a signal carrier with fingerprint peaks at approximately 1000 $cm^{-1}$ (figure 1 A). The addition of melamine in the silver growth process resulting in enlarging Raman benzene-thiol signal up to 20 times (figure 1 C).

Comparison with standard agar raman spectra [10.1117/1.JBO.17.10.107004] demonstrates that signal of target molecules is significantly higher compared to agar background. That make it possible for us to neglect its signal.

Thus, for non-melamine samples signal of benzene thiol varies in range 50 – 200 au for system with 0.2 w.% silver nitrate solution. For one with 2.0 w.% the range is 200-3000 au (not shown on a graph). The reproducible difference of the Raman signal intensity in the radial cross-section of the sample could be explained by its gradient structure. The main trend is that signal decreases upon moving far from the red nanoparticle zone to the black agglomeration zone. As we mentioned in the manuscript, the size of the particles gradually rises within distance from the beginning growth. Smaller particle size leads to the higher surface area, making it possible for more benzene-thiol to be capped. Meanwhile, bigger particles are able to host a smaller amount of benzene-thiol. This behavior is observed for both 0.2 w.% and 2.0 w.% of silver nitrate.

To explain initial signal enlargement from 3000 to 6000 AU (figure 1 B), which is typical for high concentrations of silver nitrate, we should consider the diffusion limitation of the growing process. At the very beginning of the gel phase and after the reaction has begun, there is an excess of silver nitrate and shortage of pectin. The consequence is the instant turning of pectin to precipitation and further diffusion of silver nitrate. On a small distance from the silver nitrate reservoir, its gradient is not so big, its amount is limited to diffusion. That provides enough time for ligands to diffuse toward the chemical reaction front. However, the amount of silver salt is still enough to form stable nanoparticles. The result is a higher concentration of silver nanoparticles, dark-red zone, with highest Raman signal.

While a principal behavior of a system is the same, the presence of melamine in the gel lead to the intensification of the signal up to 2 times for 2.0 w.% silver nitrate and 20 times for 0,2 w.%. Overall, we get SERS signal of the same magnitude for ten times less silver nitrate concentration, which makes it prominent for cell-culture application.

Two hypothesis were considered to describe this phenomenon. The first implies that melamine influence the process of nanoparticles formation. We suppose that melamine could interfere with a nanoparticle surface. That possibly results in both better agglomeration prevention and better formation of edges. Thus, nanoparticles of clearer size distribution and stricter grain edges tend to have better SERS signal.

Second hypothesis is that melamine is able to form complex salt with silver nitrate. Similar complex are known for silver perchlorate [10.1023/A:1009590631734] and recent works states about silver nitrate as well [10.1016/j.jssc.2019.03.038]. Thus, melamine would catch silver ions and preserve them for the reaction with thiol. At absence of melamine, these ions would be spent for nanoparticles growth, meanwhile with melamine it tend to form additional nanoparticles after drying of the film. More available for target molecule silver lead to signal enlargement.

We note, that both mechanisms are possible at the same time. While TEM data correlates with first hypothesis, additional investigation is needed and planned.

We also note, that raman signal of melamine remains on the scale of noise. Even if it possibly is significant for specific cases, it will be taken into account since its spectrum is well-known.

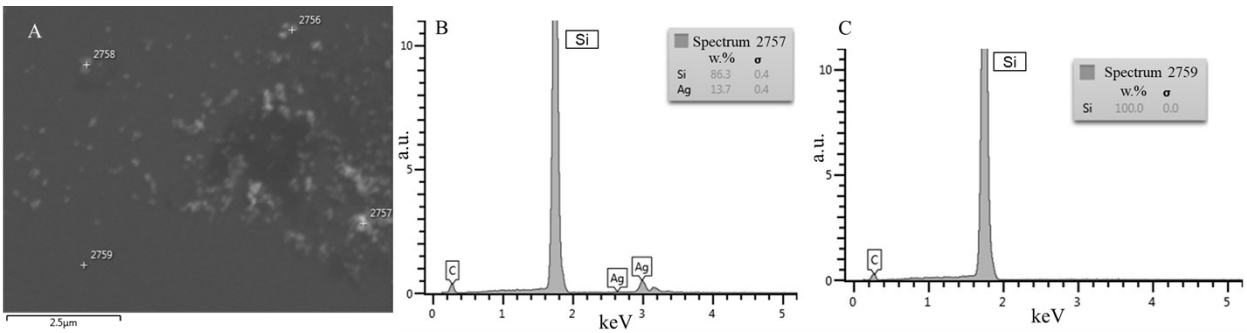


Figure 2. A. SEM image of silver particles in agar film. B. EDX spectra of point 2757, silver particles (points 2756 and 2758 are quite similar). C. EDX spectra of point 2759, pure agar film.

Images are made on scanning electron microscope Hitachi S3400N. Thin films of dried agar contained silver particles were soaked in ethanol and placed on silicon wafer. Upon complete drying, the investigation is started.

Strong band of silicon is due to silicon wafer carrier. Clear peaks of silver are observed for precipitation zones (points 2756-8). Peak of carbon states for carbon backbone of agar. Field free of silver (point 2759) shows only carbon signal. Probably, pure carbon signal is because of burning of organic non-conductive material upon high-voltage accelerated electron beam. For fresh thick material it is possible to see oxygen as well, although data are not of high reproducibility due to constant burn of organic samples.