INTERMOLECULAR INTERACTIONS OF GLUTATHIONE WITH MOLYBDENUM DISULFIDE PROBED BY LASER DESORPTION/IONIZATION MASS SPECTROMETRY

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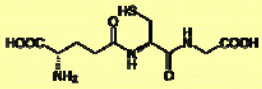
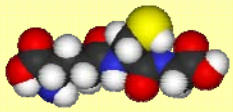
Background. An important task of modern NanoBioPhysics is development of possible biomedical applications of nano-materials, such as drug delivery. Among the requirements to drug nano-carriers there are sufficiently strong noncovalent binding of drug molecules to the carrier molecules or supramolecular complexes, as well as easy drug release at the target of the delivery, avoiding noticeable chemical modification, and biocompatibility.

A 2D nanomaterial of our current interest is a molybdenum disulfide MoS_2. In contrast to relatively inert carbon-based nanomaterials, MoS_2 contains quite active sulfur atoms which are responsible for partially negative charge of the surface of MoS_2 flakes. Such electronegative sulfur atoms can play an active role in biological processes, both noncovalent interactions and redox reactions.

The AIM of our work is to investigate interactions of MoS_2 with sulfur-containing organic molecules. As an object we have selected Glutathione, biologically active tripeptide, which exists in reduced (GSH) and oxidized "dimeric" (GSSG) states; the latter is created by formation of disulfide bridge between the cysteine moieties of the monomers.

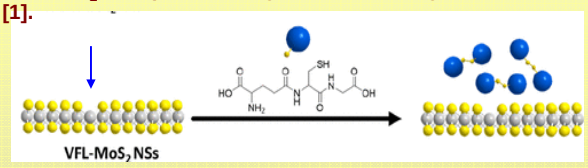




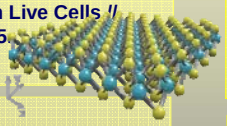
The (GSH-MoS_2) nanocomposite was prepared by sonication of aqueous mixture of GSH and MoS_2.

We have examined (GSH-MoS_2) composite by means of laser desorption/ionization (LDI) mass spectrometry.

There are literature data that GSH is dimerized in solution on the presence of MoS_2. The process may be facilitated by vacancies defects [1].

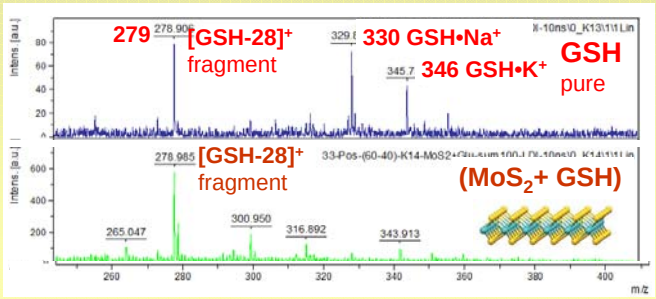


[1]. MoS_2 and $MoSe_2$ Nanosheets as Triggers for Glutathione Dimerization in Solution and Glutathione Oxidation in Live Cells // *ACS Applied Nano Materials*. (2022) 5 (8), 10583-10595. DOI: 10.1021/acsanm.2c01920



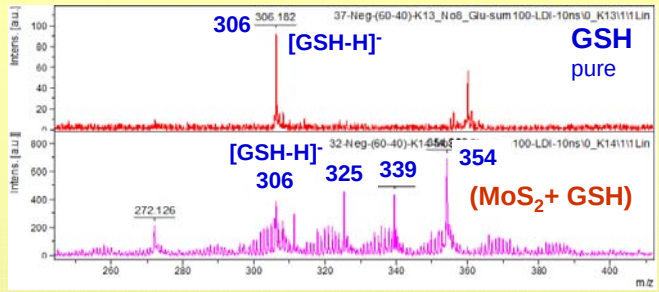
Laser Desorption/Ionization Mass Spectrometry of (GSH + MoS_2) composite

Positive ion LDI mass spectra.



Pure GSH is represented by cationized species and abundant fragment at *m/z* 279. This fragment is dominant in the mass spectrum of the (GSH+MoS_2) composite. At the same time a cationized dimer $[GSSG+Na]^+$, m/z 635, was recorded. This hints at some transformations of the GSH on the MoS_2 surface.

Negative ion LDI mass spectra.

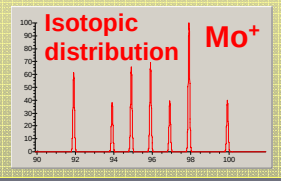


The deprotonated GSH, $[GSH - H]^-$, m/z 306, is characteristic of pure GSH. In the spectra of (GSH+MoS_2), however, several peaks which can be attributed to $[GSH+H_2O]^-$,m/z 325, $[GSH+S]^-$, m/z 339, and $[GSH+47]^-$, presumably $[GSO_3]^-$, m/z 354, were recorded.

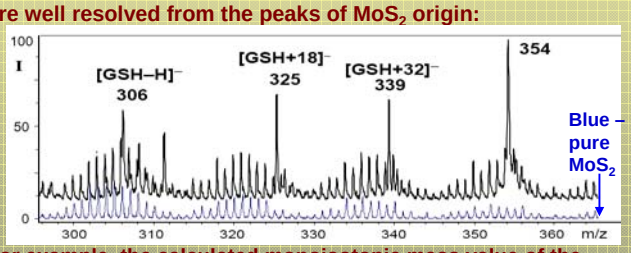
Such a set of peaks different from solely molecular ions of GSH, points to a possibility of both physical and chemical nature of interactions of GSH with MoS_2.

Note for mass spectra interpretation.

Mo is a polyisotopic element, it has 7 isotopes in 92-100 a.u. range. Clusters $Mo_xS_yO_z$ are sputtered from MoS_2 sheets under LDI in the negative ion mode.



From the point of view of mass spectrometry basics, it is of interest that in the obtained spectra the organic-related peaks are well resolved from the peaks of MoS_2 origin:



For example, the calculated monoisotopic mass value of the $[GSH+S]^-$, 339.056 (or $[GSH+2O]^-$, 339.073) is located between two peaks of $Mo_2S_4O^-$ cluster distribution 338.694 and 339.694.

LDI mass spectrometric experiments were performed with MALDI-TOF Autoflex II LRF20 instrument (Bruker Daltonics, Germany).

Gratitude to the Center for collective use of scientific instruments/equipment

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