MASS SPECTROMETRIC PROBING OF NANOCOMPOSITE OF METHYLENE BLUE WITH MOLYBDENUM DISULFIDE FLAKES

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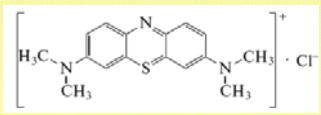
NOVEL IDEA (from literature) :

Recently, in the search of new nanotechnology-based oncotherapy approaches, it was proposed to evaluate multifunctional nanoplatforms which would provide several different mechanisms of anticancer action simultaneously [1]. Guided by this trend, we considered a combination of methylene blue (MB) dye applied in photodynamic therapy (PDT) with MoS_2 promising in photothermal therapy (PTT).



The (MB-MoS_2) nanocomposite was prepared by sonication of the components mixture in water, which is known to exfoliate MoS_2 to flakes available for adsorption of organic compounds.

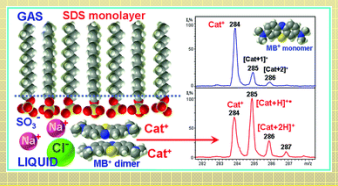
[1] Q. Wang et al, Multifunctional Nanoplatform for NIR-II Imaging-Guided Synergistic Oncotherapy. Int. J. Mol. Sci. 24, 16949 (2023).

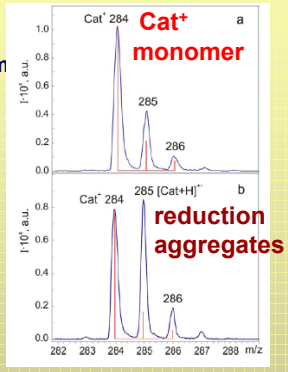
Background. Laser Desorption/Ionization (LDI) mass spectrometry was selected to probe (MB+MoS_2) nanocomposite basing on our earlier observations of the sensitivity of certain mass spectral parameters to the state of MB at the nanostructured substrates, its aggregation and redox transformations [2].

[2]. Kosevich M.V., Boryak O.A., Chagovets V.V., Shelkovsky V.S., Pokrovskiy V.A. Interactions of biologically active redox-sensitive dyes with nanomaterials: Mass spectrometric diagnostics // Nanobiophysics: Fundamentals and Applications. Singapore: Pan Stanford (2016)

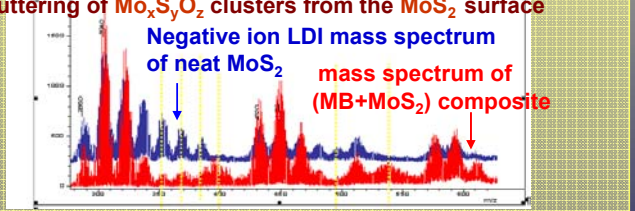
It was revealed that monomeric adsorptionof MB^+ cation on various substrates is reflected in the spectrum of intact cation(m/z 284), while aggregation promotes reduction of MB and appearance of its reduction product (m/z 285).

Example: MB on SDS layer:





Adsorption of organic compounds on MoS_2 flakes affects sputtering of $Mo_xS_yO_z$ clusters from the MoS_2 surface



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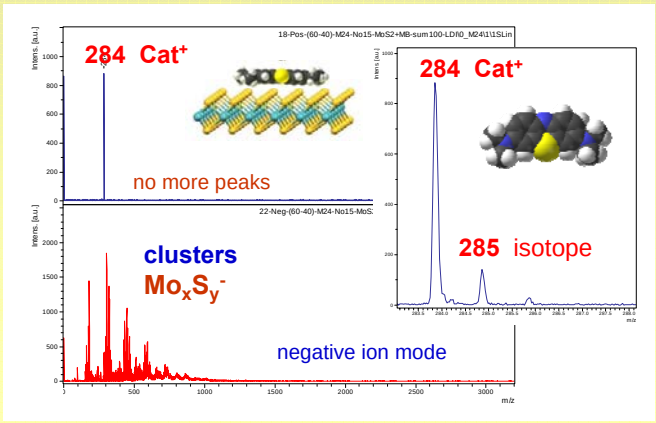
Laser Desorption/Ionization Mass Spectrometry of (MoS_2 + Methylene Blue) composite

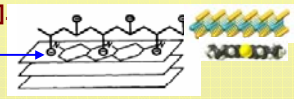
The main result: characteristic LDI mass spectra obtained in the positive and negative ion modes:



In the LDI mass spectra of the (MB-MoS_2) dry sample, recorded in positive ion mode, a single abundant peaks envelope with isotopic distribution characteristic of intact cation of MB^+ was present. This feature correlates with the monomeric adsorption of MB^+ cations on the nanostructured surfaces.

Discussion. Idea. It is presumed that MB cations are adsorbed on the partially negatively charged surface of MoS_2 loosing the chlorine anion of the MB organic salt. Thus a kind of a "SALT" of MB^+ cation and MoS_2 as an extended anion is formed. Formation of "salts" of organic cations and polymeric poly-anions was expressed earlier [3].

[3] А.О. Шийчук. Спектральні перетворення барвників під час взаємодії з речовинами, що містять полігони // Колоїдна Хімія



We propose salt-like structure formation with negatively charged nanoflakes as the anion. Existence of the "preformed" cations on the MoS_2 surface provides their easy desorption by laser irradiation under LDI conditions.

Biomedical implications.

PDT: It is known that namely monomeric form of MB is required for realization of a PDT mechanism of singlet oxygen production.

PTT: The efficiency of the cations desorption increased dramatically with increase of the irradiating laser power, which was caused, obviously, by increase of heating of the exfoliated MoS_2 flakes. This effect is related to PTT potential of MoS_2 . Thus, two above described features of the LDI mass spectra may be used for evaluation of some properties of the MB-MoS_2 as a nanoplatform.

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