MASS SPECTROMETRIC ASSESSMENT OF TRANSITION METAL DICHALCOGENIDES FUNCTIONING AS NANOZYMES

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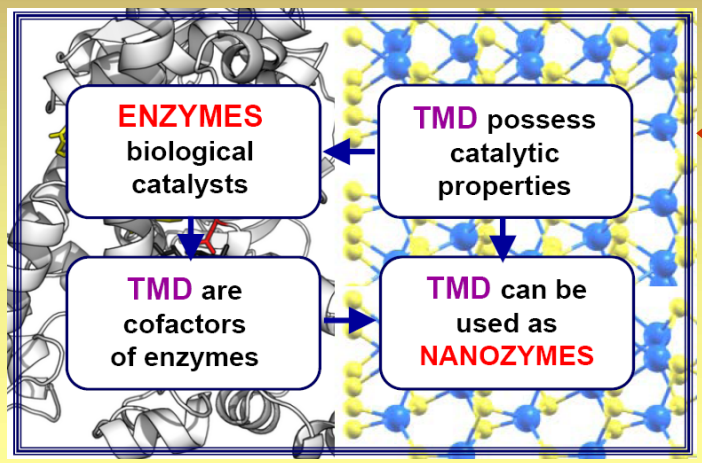


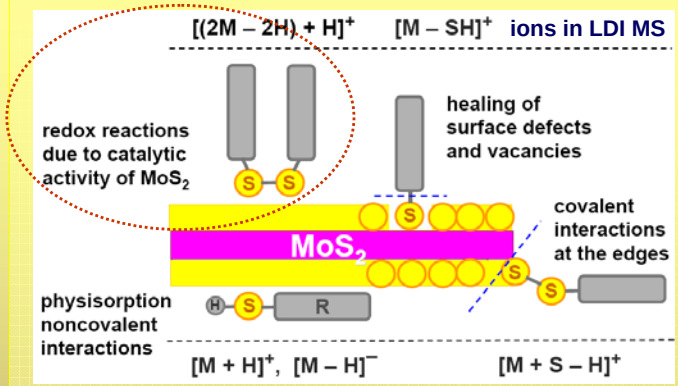
Transition metal dichalcogenides (TMD) exhibit catalytic activity in biological systems, being constituents of enzymes' cofactors. A trend in modern nanobiotechnology is the substitution of biological enzymes with their simpler and cheaper inorganic analogues, called nanozymes [1]. TMD-based 2D nanomaterials are promising for this application [2, 3].

1. M. Zandieh, J. Liu, Advanced Materials, 36(10) e2211041 (2023).
2. H. Wei, E. Wang, Chem Soc Rev. 42(14) 6060-93 (2013).
3. N. Saravanan, S. Bajhal, J. Thinakaran, A. Sundaramurthy, Nanomedicine, 20(13) 1621 (2025).

In this communication, we evaluate the catalytic redox activity of 2D TMD MoS_2 and WS_2 in relation to a set of biologically significant organic molecules – amino acids, nitrogen bases, dyes, and simple thiols – based on information obtained using the laser desorption/ionization (LDI) mass spectrometric experimental technique. LDI permits the desorption of components and products of redox reactions directly from the surface of 2D nanosheets; the high sensitivity of the method allows detection of small quantities of substances.

The strongest catalytic effect of MoS_2 was observed in cases of MoS_2 interactions with organic compounds that contain thiol groups. The main effect is the promotion of redox transformations of organics.

A scheme of thiols interactions with a TMD nanosheet



EXPERIMENTAL

Preparation

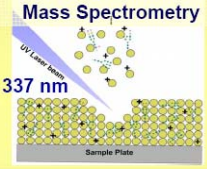
Ultrasound treatment of the mixture of the components in water, 1700 kHz

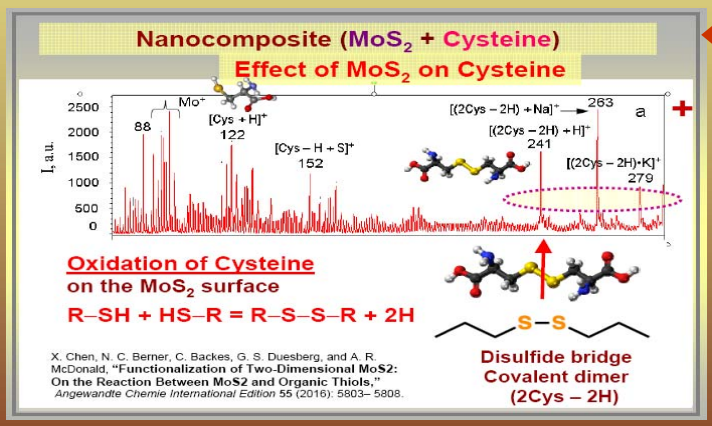
MoS_2 powder > 2μm

Exfoliation to nanosheets built of several layers of MoS_2 . Cysteine functionalize MoS_2.

Characterization

Laser Desorption/Ionization Mass Spectrometry





For the cysteine amino acid, tripeptide glutathione, thioderivatives of nitrogen bases, and thioglycerol the oxidation reaction was catalyzed at the MoS_2 surface, resulting in the formation of covalent dimers bound by a disulfide bond. Interestingly, in the mixture of cysteine with thioglycerol, a heterodimer of two different thiols was formed.

However, for practical applications of TMD as nanozymes for definite types of reactions, the conditions for the elimination of some accompanying effects are to be established. Namely, the deepening of organics transformations may lead to fragmentation and destruction of organic molecules, which products are also observed in the mass spectra of glutathione and some polymers. In addition to interactions at the 2D planes, organic molecules can bind to the edges of 2D nanosheets (see Scheme); the outcomes of these interactions differ from those with the surface.

An example for LDI mass spectrometric identification of the redox products of amino acid Cysteine transformation promoted by MoS_2 which can be considered as a "NANOZYME" for these reactions.

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