“Poor man’s” depth profiling: microscopy and laser desorption/ionization mass spectrometry of a thin film of (MoS_2 + PEG + thioglycerol) system

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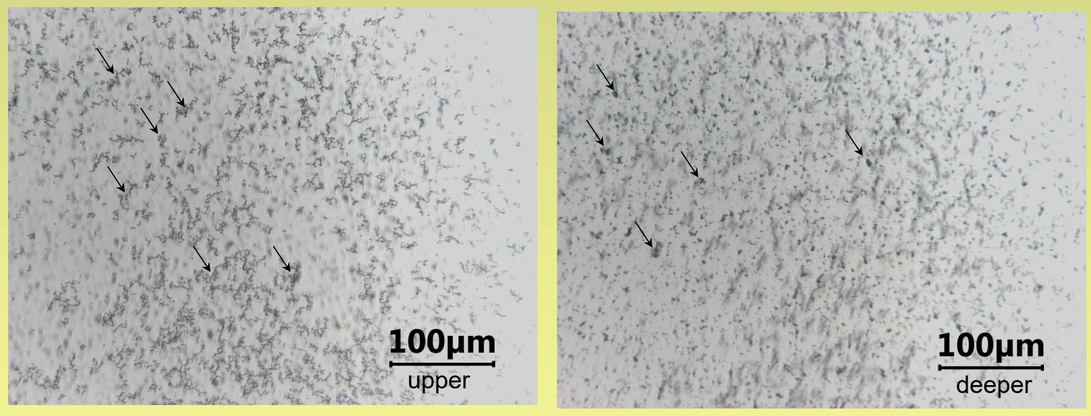
A jocular term, “poor man’s” experimental methods, was coined to refer to a relatively simple technique that permits obtaining some experimental results similar to those expected from more intricate ones. In this report, we present data on distinguishing the upper and bottom layers, i.e., a simplified “depth profiling” of a thin film of (MoS_2 + PEG +TG) (TG = thioglycerol) sample probed by optical microscopy and laser desorption/ionization (LDI) mass spectrometry.

The triple mixture of MoS_2 inorganic nanomaterial, the organic polymer PEG-600, and thioglycerol (as an exfoliation-assisting agents) intended for nanocomposite preparation was treated by ultrasound in an aqueous medium.

Dried (MoS_2+PEG+TG) film was probed by the LDI mass spectrometry using increasing laser power (LP) value.

At larger LP lager volume (and depth) of the film is affected.

OPTICAL MICROSCOPY IMAGES of (MoS_2 + PEG + TG)



Inspection of the dehydrated film (about 0.1 mm thick) showed that the image changes qualitatively with the change of focusing of the optical lens: upper layer of the film was enriched by chains of particles, virtually bound due to the PEGylation effect of PEG (left); focusing on the lower layer of the transparent film revealed small separate particles (right).

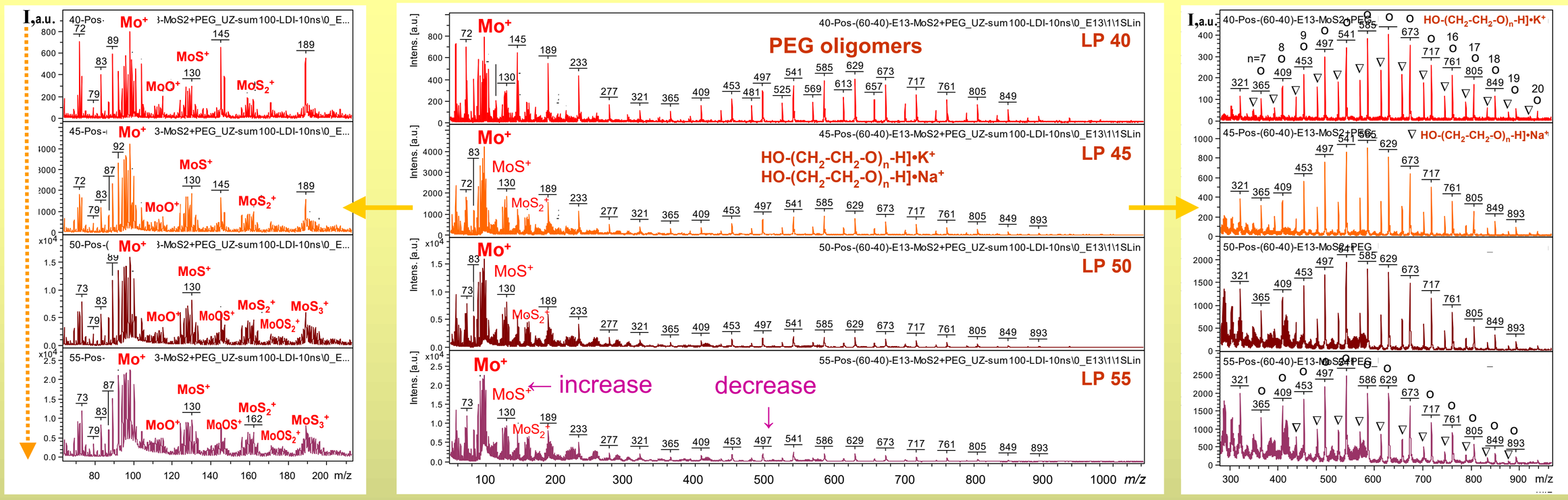
Laser Desorption / Ionization Mass Spectrometry of (MoS_2+PEG+TG)

Mass spectra were recorded subsequently, increasing the laser power value: 40, 45, 50, 55 % of the maximum LP.

The total ion current and absolute intensities of all ions in the spectra increased with the increase of LP.

Bell-shaped distribution of cationized oligomers corresponded to PEG-600 (right). Mo^+, MoO^+, MoS^+, MoS_2^+ ions were sputtered from MoS_2 (left).

Overview spectra (center).



While the total ion current grows with LP increase, the redistribution of abundances of peak groups associated with MoS_2 and PEG takes place. At a relatively low laser pulse power (LP 40), ensuring desorption mode from the surface layer, the peaks group characteristic of PEG dominated the spectrum, while the signals connected MoS_2 were comparatively low. Such a spectral pattern agrees with the surface localization of MoS_2 particles covered with PEG. A substantial increase in laser power (up to LP 50-55) provides the atomization of deeper layers of the sample film. PEG-related spectrum is substantially suppressed in favour of noticeable growth of MoS_2-related ions.

Observation of Mo^+ and its clusters with sulfur in the positive ion mode (left) is of practical significance, since it points to a certain distortion of MoS2 by PEG, which was earlier neglected in the creation of (MoS_2+PEG) composites. MoS_2-related clusters were earlier recorded in the negative ion mode only for pristine MoS_2.

Thus, the LDI with varied LP can probe the layered structure of the (MoS_2+PEG+TG) dried film, i.e., mimic “depth profiling”: PEG is mainly desorbed from the surface layer at lower LP, and more MoS_2 ions are extracted from the bottom layer at higher LP. The present observation is of practical value for analytical applications of LDI mass spectrometry.

EXPERIMENTAL

Nanocomposite was prepared by sonication of the three components in an aqueous medium using a piezoelectric oscillator generating a 1700 kHz frequency. LDI mass spectrometric experiments were performed with a MALDI-TOF Autoflex II LRF20 instrument (Bruker Daltonics, Germany), applying a UV laser operating at 337 nm.

CONCLUSION: Variation of laser power in LDI permits to mimic a “depth profiling” of a multilayer film.

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