Black phosphorus enriched matrix-assisted laser desorption ionization (MALDI) matrices for increased sensitivity of mass spectrometric detection of biomolecules: Spectrophotometric, fluorimetric, and mass spectrometric study

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## ABSTRACT

We studied the effect of black phosphorus (BP) or phosphorene enriched matrices for ionization of biomolecules in mass spectrometry. It was observed that BP enriched a-cyano-4hydroxycinnamic acid (CHCA) matrix enhances the intensity of mass spectra significantly in comparison to pure CHCA matrix. In case of amino acids (AAs), the intensities of mass spectra recorded from glycine (Gly), leucine (Leu), phenylalanine (Phe), and tryptophan (Trp) enhanced 26, 50, 30, and 8 times, respectively. The intensities of mass spectra of bradykinin 1-7, angiotensin II, [glu-1]-fibrinopeptide, adrenocorticotropic hormone 1-17 (ACTH 1-17), and ACTH 18-39 standard peptides (Pep) have increased by 35, 28, 8, 4, and 20 times, respectively. The intensities of mass spectra generated from synthetic peptides: A (PRGFSCLLLLTGEIDLP), B (PRGFSCLLLLCGEIDLP), C (PRGFSCLLLLTSEIDLP), and D (MAPRGFSCLLLLTGEIDLPVKRRA) have enhanced 12, 8, 11, and 6 times, respectively. In addition, discrimination of three different cancer cell lines ID8 SCR (mouse ovarian surface epithelial cell line), A2780, and SKOV3 (human ovarian cancer cell lines) has improved from their mass spectra were measured using BP enriched SA matrix. Further, to find the cause of enhanced ionization, interaction of BP fine particles with amino acids or peptides was also investigated using UV-vis spectrophotometry and fluorimetry. It was found that amino acids

(Phe and Trp) or peptides containing aromatic rings are interacting with black phosphorus surface (micro or fine BP particles), while Gly or Leu amino acids (containing no aromatic ring) are not. However, this interaction is not connected with their increased ionization using BP enriched CHCA matrix. In the contrary, the ionization of Gly and Leu using BP enriched CHCA matrix is higher than that one observed for Phe and Trp. Therefore, enhanced ionization of effect of BP can be mostly explained by surface-assisted laser desorption ionization (SALDI).

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