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Supporting Information

Layer-by-layer assembled MoS_2 thin film as an efficient platform for laser desorption/ionization mass spectrometry analysis of small molecules

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Surface functionalization of glass coverslips

#2 glass coverslips were immersed in piranha solution (H_2SO_4:H_2O_2 (30%) = 3:1) (warning: piranha solution is extremely toxic and corrosive) for 10 min at 125 °C, washed with water and ethanol, and dried under a stream of nitrogen. The substrates were immersed in a 10 mM toluene solution of 3-APTES for 30 min, sonicated in toluene for 2 min, rinsed with ethanol and water, and dried under a stream of nitrogen.

Synthesis of multi-walled carbon nanotube (MWCNT)

MWCNT was purchased from the Alfa Aesar. 100 mg of MWCNT was dispersed in a mixture of concentrated nitric acid and sulfuric acid (1:3), sonicated for 6 h and purified by repeated centrifugation and washing with water.

Synthesis of graphene oxide (GO)

Natural graphite was purchased from Aldrich. GO was synthesized by the otherwise reported method.[1]

Synthesis of Au nanoparticles (NPs)

Au NPs functionalized with alkanethiol with triethylene glycol terminal group were synthesized by our reported method.[2]

Synthesis of Fe_3O_4 NPs

Fe3O4 NPs functionalized with dopamine derivatives with triethylene glycol and quaternary ammonium terminal group were synthesized by our previously reported method.[3]

Synthesis of benzylpyridinium salt

7.8 g of benzyl bromide (45.5 mmol) was added to 3.0 g of pyridine (37.9 mmol) in a glass vial with stirring. The reaction was carried out at 50 ^{o}C overnight. The formed precipitate was washed with diethyl ether, filtered, and washed with diethyl ether (95% yield). The BP was dissolved in methanol at 1 mM for LDI-MS analysis.

Characterization

The size and morphology of MoS_2 nanoflake was observed by using a JEOL 200FX transmission electron microscopy (TEM). The thickness of MoS_2 nanoflake was examined by using a DI dimension 3100 atomic force microscopy (AFM). The surface morphology of $[MoS_2/PAAH]_{1-3}$ films was analyzed with a FEI Magellan 400 field emission scanning electron microscopy (FE-SEM). UV-vis spectra of MoS_2 nanoflake and $[MoS_2/PAAH]_{1-3}$ films were recorded with SpectraMax M2 (Molecular Devices, USA). X-ray photoelectron spectroscopy (XPS) analysis of MoS_2 nanoflake was carried out by using a Quantum 2000 scanning ESCA microprobe (Physical Electronics, USA). All LDI-MS analyses of small molecules with MoS_2 nanoflake and $[MoS_2/PAAH]_{1-3}$ films were performed by using a Bruker Autoflex III (Bruker Daltonics, Germany) equipped with a Smartbeam laser (Nd:YAG,

355 nm, 120 μJ, 100 Hz, 50 μm of spot diameter at target plate) in both positive and negative reflection mode. The accelerating voltage was 19 kV, and all spectra were obtained by averaging 500 laser shots with 48 μJ laser power unless otherwise indicated.

Figure

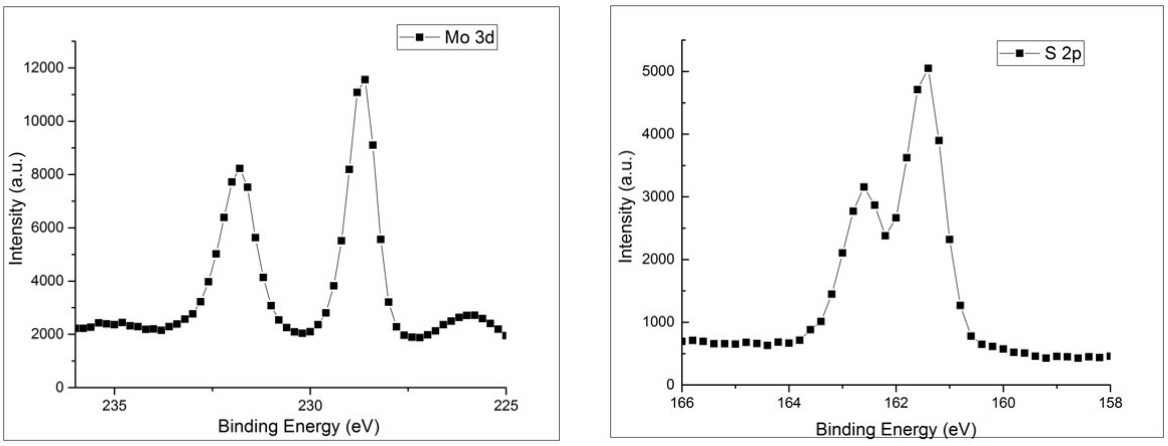

Figure S1. XPS spectra of liquid phase exfoliated MoS_2 nanoflake. The Mo 3d XPS spectrum of MoS_2 nanoflake showed two typical Mo^{4+} $3d_{5/2}$ and Mo^{4+} $3d_{3/2}$ peaks at 229.3 and 232.6 eV, respectively. A broad peak at around 236 eV corresponds to Mo^{6+} $3d_{5/2}$ from Mo oxidation. Those peaks are matched with the expected values for Mo^{4+} in MoS_2 and s small peak at around 236 eV corresponds to Mo^{6+} $3d_{5/2}$ from Mo oxidation. The S 2p peak of MoS_2 nanoflake consists of a single doublet peak of $2p_{1/2}$ and S $2p_{3/2}$ at 163.4 and 162.3 eV, corresponding to the S^{2-} type present in MoS_2.

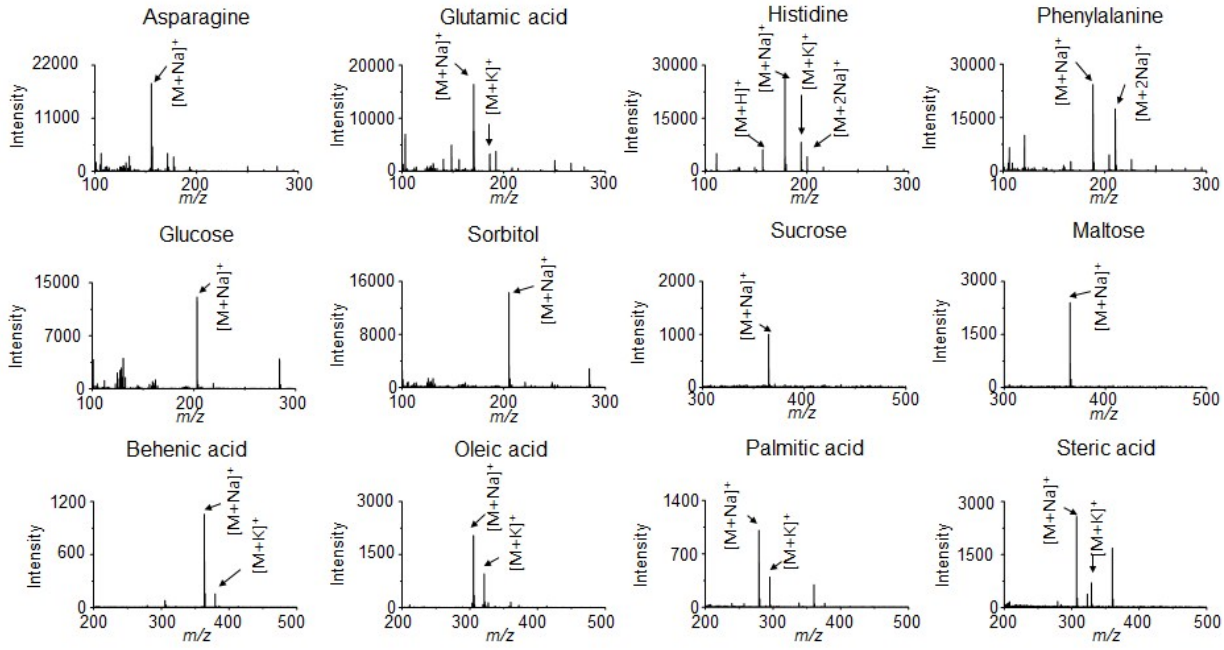

Figure S2. Mass spectra of amino acids (asparagine: *m/z* 154 $[M+Na]^+$; glutamic acid: *m/z* 169 $[M+Na]^+$, 186 $[M+K]^+$; histidine: *m/z* 156 $[M+H]^+$, 177 $[M+Na]^+$, 193 $[M+K]^+$, 199 $[M+2Na]^+$; phenylalanine: *m/z* 188 $[M+Na]^+$, 210 $[M+2Na]^+$;), saccharides (glucose: *m/z* 202 $[M+Na]^+$; sorbitol: *m/z* 204 $[M+Na]^+$; sucrose: *m/z* 364 $[M+Na]^+$; maltose: *m/z* 364 $[M+Na]^+$), and fatty acids (behenic acid: *m/z* 362 $[M+Na]^+$, 378 $[M+K]^+$; oleic acid: *m/z* 304 $[M+Na]^+$, 320 $[M+K]^+$; palmitic acid: *m/z* 278 $[M+Na]^+$, 294 $[M+K]^+$; Stearic acid: *m/z* 306 $[M+Na]^+$, 322 $[M+K]^+$) obtained with MoS_2 nanoflake under positive ionization mode. M is corresponding to the exact mass of each analyte.

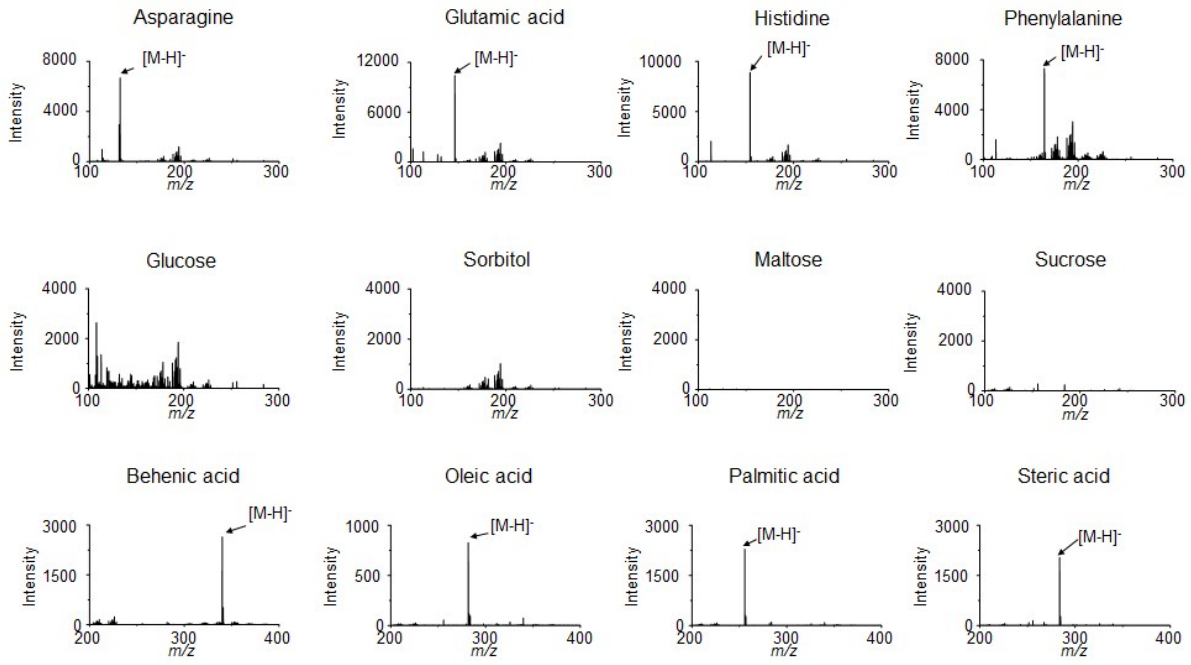

Figure S3. Mass spectra of amino acids (asparagine, glutamic acid, histidine and phenylalanine), saccharides (glucose, sorbitol, sucrose and maltose), and fatty acids (behenic acid, oleic acid, palmitic acid and stearic acid) obtained with MoS_2 nanoflake under negative ionization mode. M is corresponding to the exact mass of each analyte.

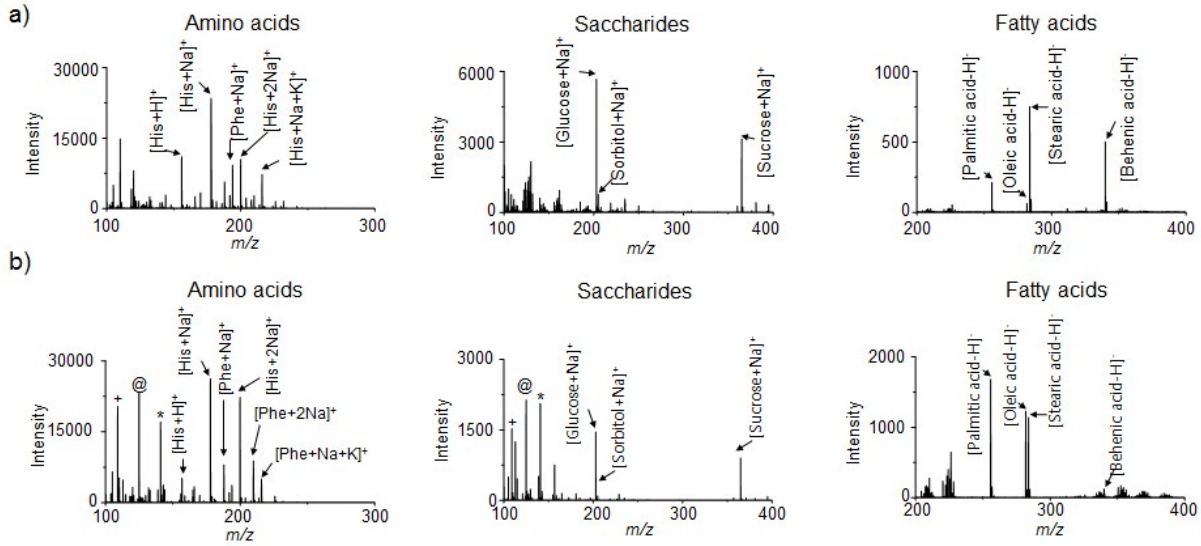

Figure S4. Mass spectra of amino acid mixture (asparagine, glutamic acid, histidine and phenylalanine), saccharide mixture (glucose, sorbitol, sucrose and maltose), and fatty acid mixture (behenic acid, oleic acid, palmitic acid and stearic acid) in PBS obtained with MoS_2 nanoflake under their preferential ionization mode. The concentration of each mixture was 1 nmol. The symbol +, @ and * respectively correspond to $[MoO]^+$, $[MoO_2]^+$ and $[MoO_3]^+$ ions.

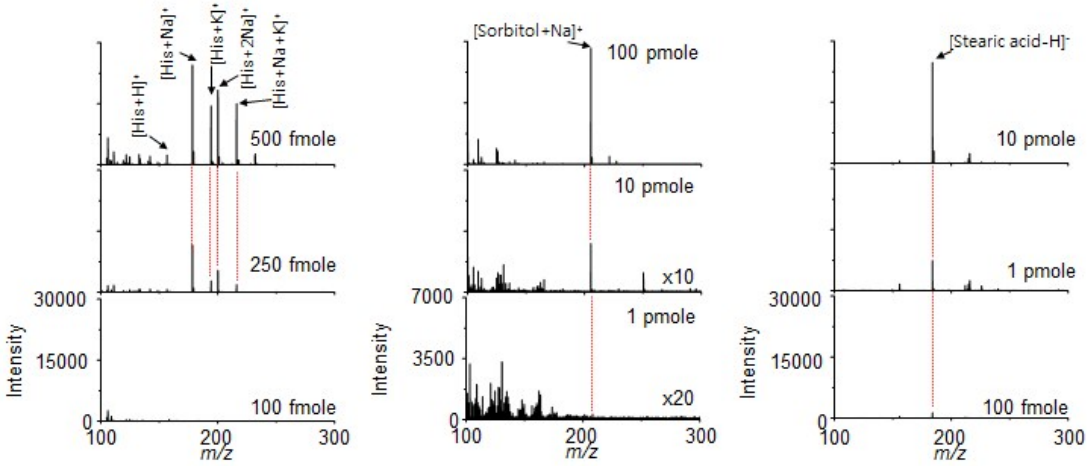

Figure S5. Mass spectra of differently concentrated histidine, sorbitol and stearic acid obtained with MoS_2 nanoflake under their preferable ionization mode. Amino acids and saccharides preferred positive ionization mode but fatty acids preferred negative ionization mode.

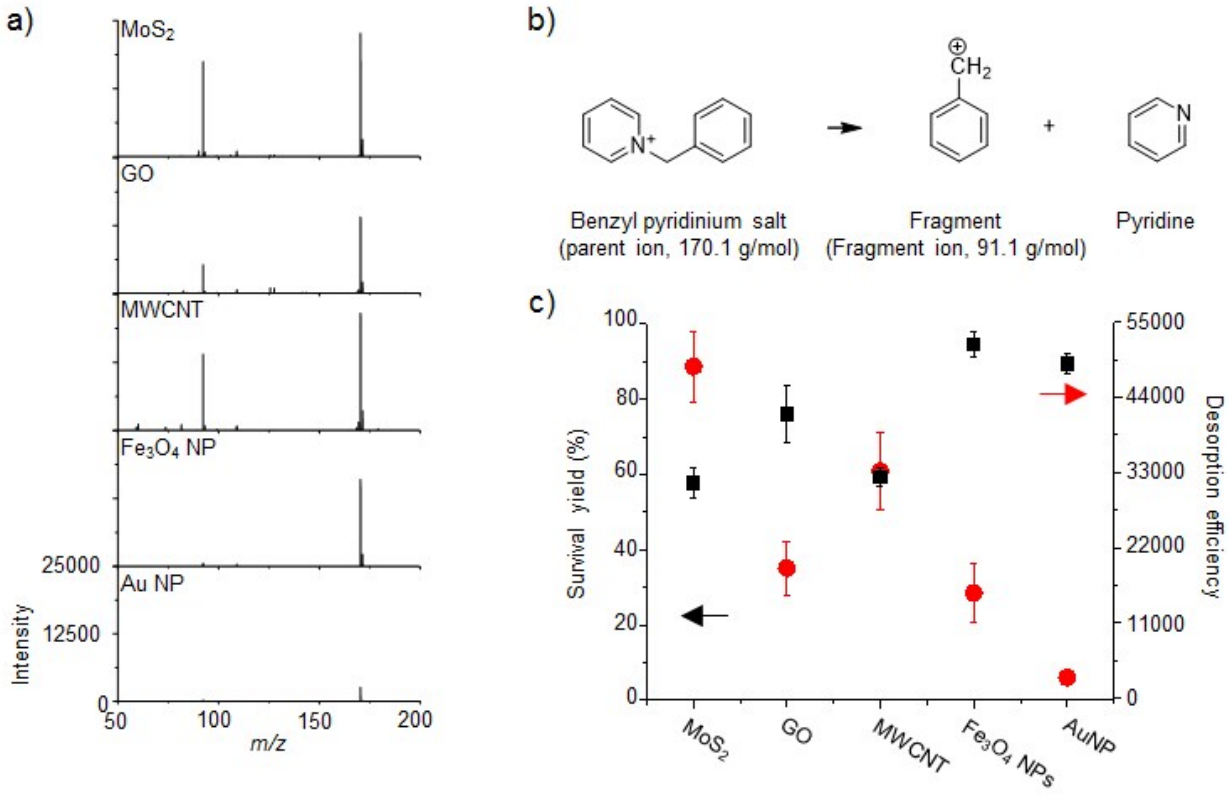

Figure 6. a) Mass spectra of BP obtained with MoS_2 nanoflake, GO, MWCNT, Fe_3O_4 and Au NPs. b) the fragmentation reaction of BP molecule during LDI-MS analysis. c) The DE and SY values of MoS_2 nanoflake, GO, MWCNT, Fe_3O_4 and Au NPs.

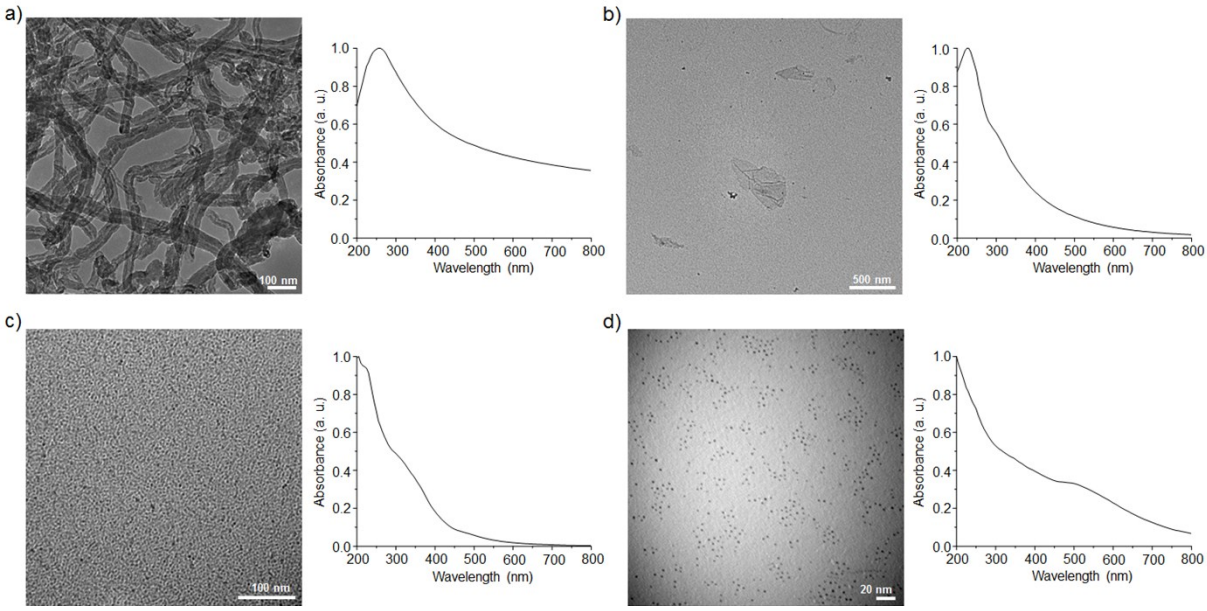

Figure S7. TEM images and UV-vis spectra of MWCNT (a), GO (b), Fe_3O_4NPs (c), and AuNPs (d).

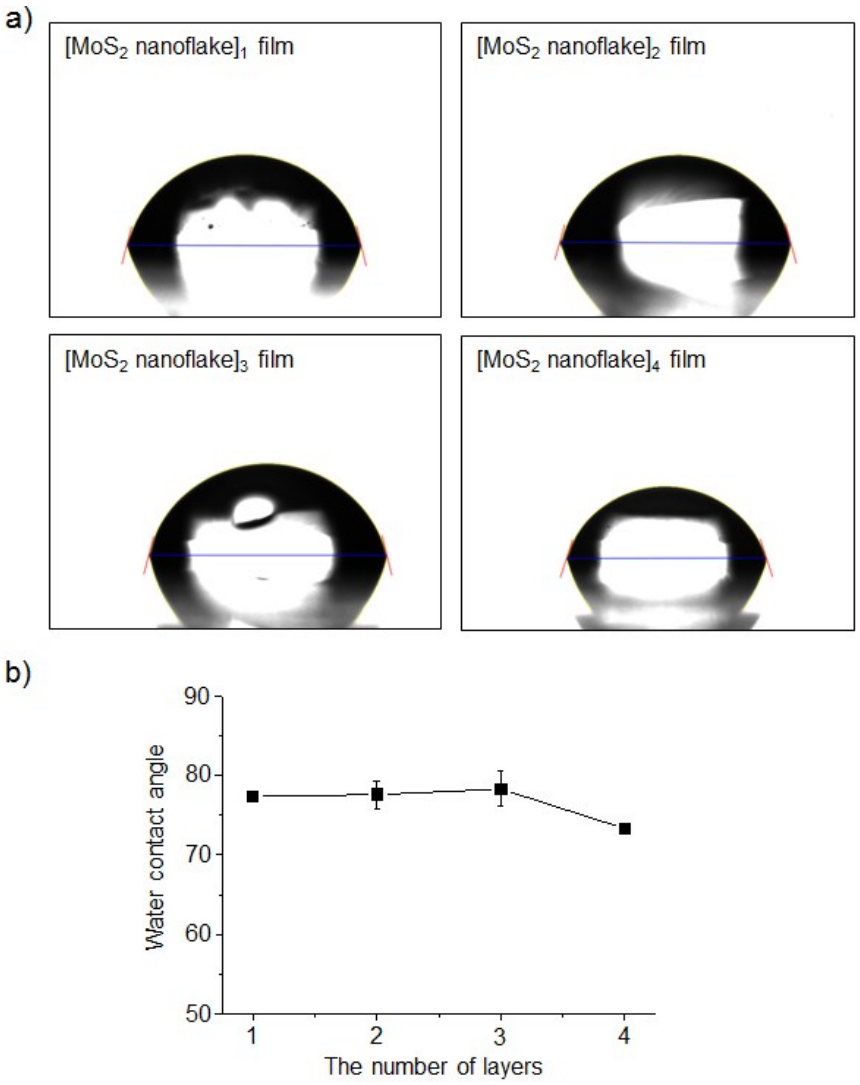

Figure S8. Water contact angles on $[MoS_2\ nanoflake]_{1\text{-}4}$ films (a, b).

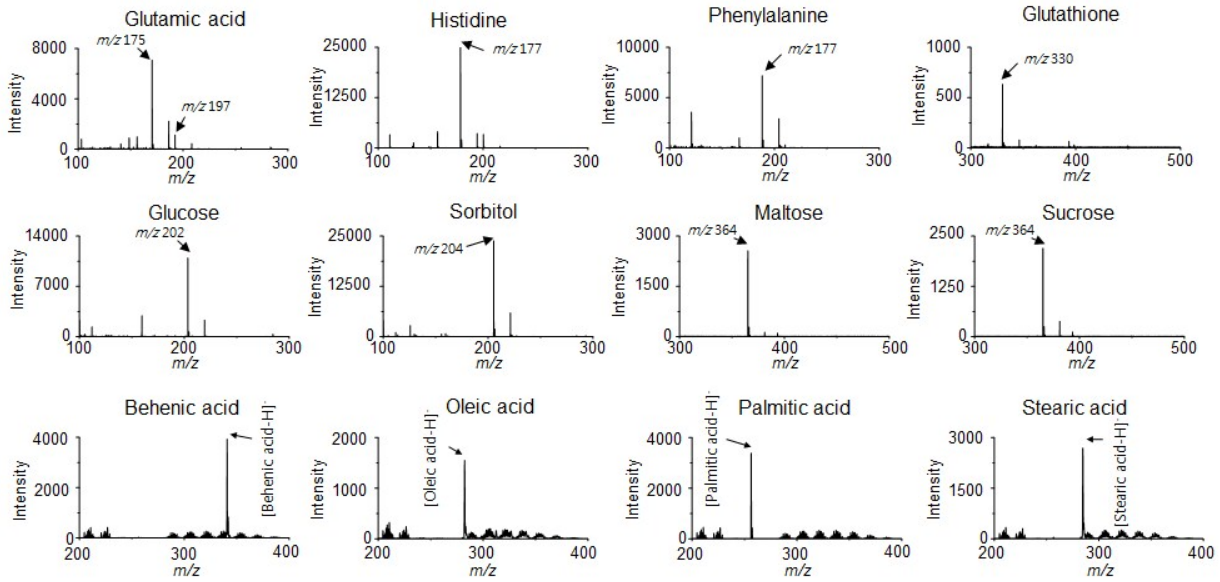

Figure S9. Mass spectra of amino acids, saccharids and fatty acids dissolved in DI water obtained on the $[MoS_2$ nanoflake$]_3$ films under their preferable ionization mode.

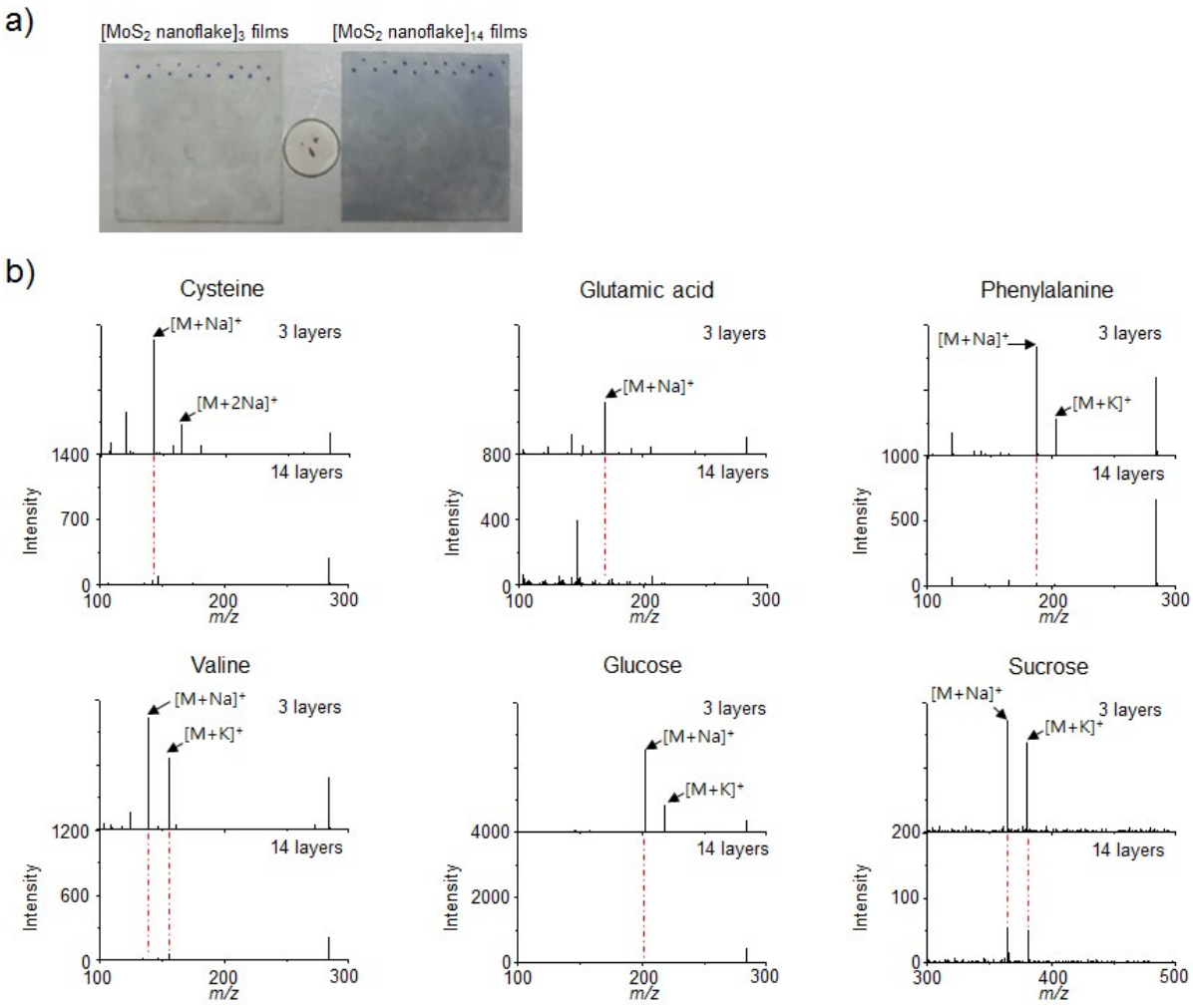

Figure S10. Photographs of [MoS_2 nanoflake]$_3$ and [MoS_2 nanoflake]$_{14}$ films mounted on the plate for LDI-MS analysis (a) and mass spectra of small moleclues obtained on the [MoS_2 nanoflake]$_3$ and [MoS_2 nanoflake]$_{14}$ films under the same analytical conditions (b).

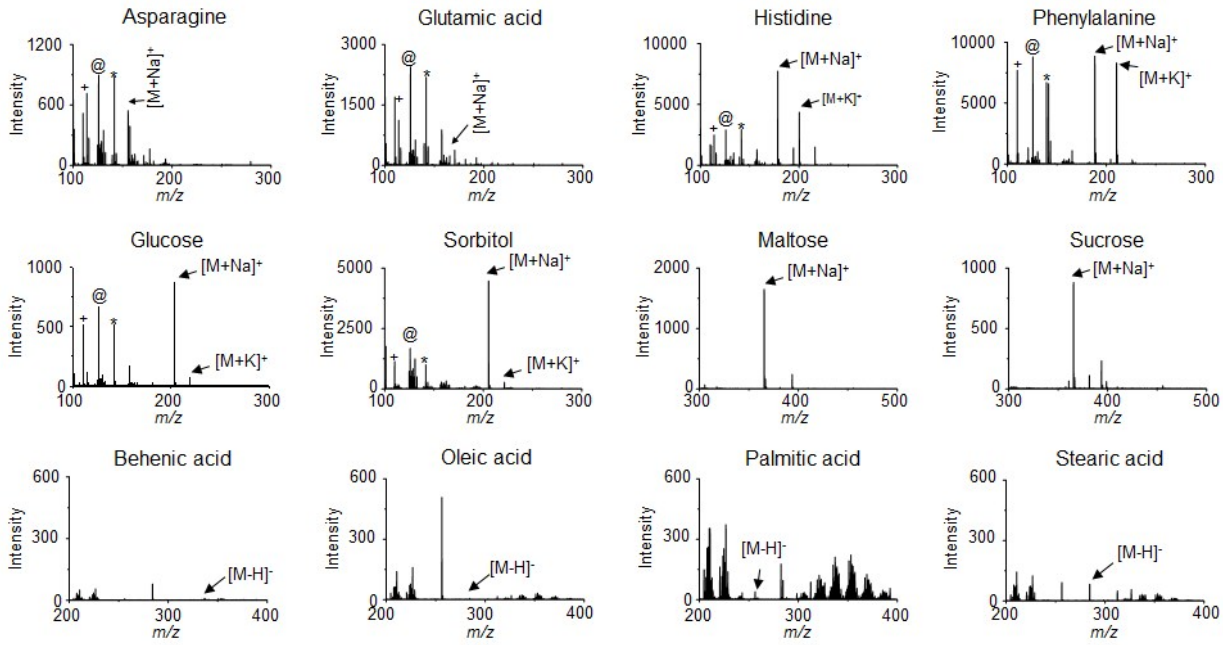

Figure S11. Mass spectra of amino acids (asparagine, glutamic acid, histidine and phenylalanine), saccharides (glucose, sorbitol, sucrose and maltose), and fatty acids (behenic acid, oleic acid, palmitic acid and stearic acid) dissolved in PBS obtained on $[MoS_2$ nanoflake$]_3$ films under their preferential ionization mode. The concentration of each small molecule was 1 nmol. The symbol +, @ and * respectively correspond to $[MoO]^+$, $[MoO_2]^+$ and $[MoO_3]^+$ ions. The emergence of $[MoO_n]^+$ ions in the mass spectra of small molecules dissolved in PBS is likely due to the oxidation of MoS_2 nanoflakes in PBS containing concentrated salts,[4] but this hypothesis requires further work to study the aging effects of MoS_2 nanoflakes in buffered solutions.

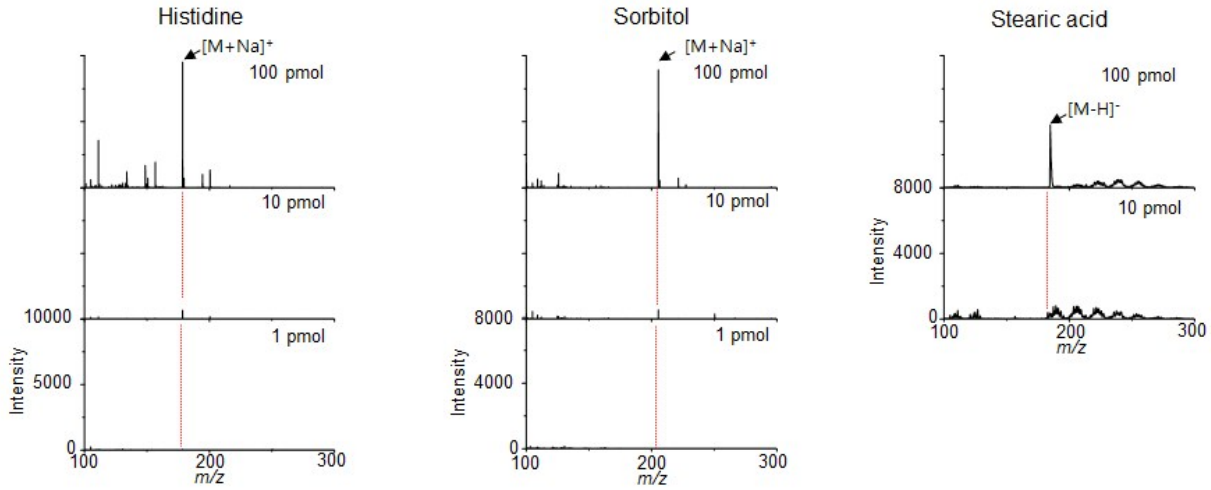

Figure S12. Mass spectra of differently concentrated histidine, sorbitol and stearic acid obtained on the $[MoS_2$ nanoflake$]_3$ films under their preferable ionization mode.

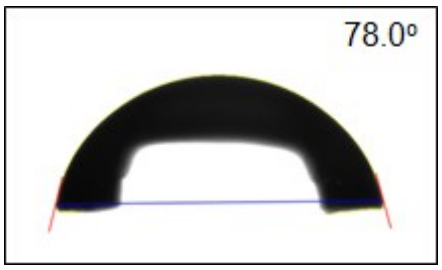

Figure S13. Water contact angle on 1H,1H,2H,2H-perfluorodecanethiol modified [MoS_2 nanoflake]$_3$ films.

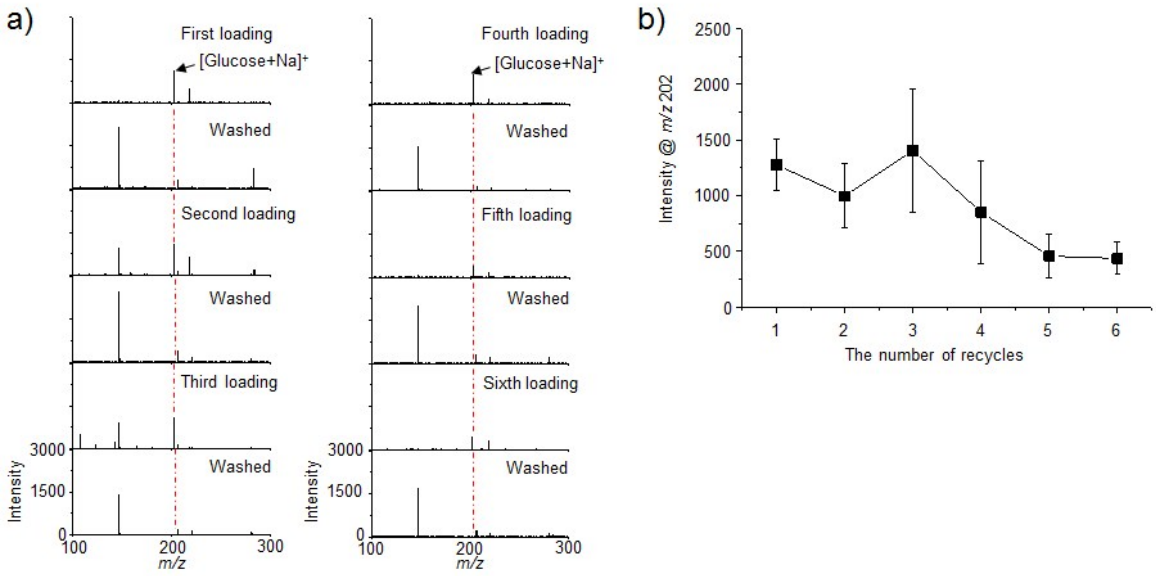

Figure S14. a) Mass spectra of glucose obtained on the [MoS_2 nanoflake]$_3$ film with repeated loading of 1 nmol glucose and washing with water and ethanol under positive ionization mode. b) the change of mass peak intensity of cationic adduct of glucose with Na^+ ion at *m/z* 202 was plotted as a function of the number of recycles. For the recycling experiments, 1 nmol glucose was spotted on the [MoS_2 nanoflake]$_3$ film, subjected to LDI-MS analysis, washed with water and ethanol, and then subjected to LDI-MS analysis. This cycle was repeated to six cycles.

References

1. Y. –K. Kim, D. –H. Min, *ACS Appl. Mater. Interfaces.* 2012, **4**, 2088.
2. A. L. Marsico, B. Duncan, R. F. Landis, G. Y. Tonga, V. M. Rotello, R. W. Vachet, *Anal. Chem.* 2017, **89**, 3009.
3. B. Yan, Y. Jeong, L. A. Mercante, G. Y. Tonga, C. Kim, Z. J. Zhu, R. W. Vachet, V. M. Rotello, *Nanoscale*, 2013, **5**, 5063.
4. Z. Wang, A. von dem Bussche, Y. Qiu, T. M. Valentin, K. Gion, A. B. Kane, R. H. Hurt, *Environ. Sci. Technol.* 2016, **50**, 7208.