

Supporting Information

Fabrication of Alternating Multilayer Films of Graphene Oxide and Carbon Nanotube and Its Application in Mechanistic Study of Laser Desorption/Ionization of Small Molecules

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Supporting Information

APTES functionalization of a glass substrate

The #2 glass cover slip was treated in Piranha solution for 10 min at 125 °C, washed with water and ethanol, and dried under a stream of nitrogen. The treated substrates were immersed in a 10 mM anhydrous toluene solution of APTES for 30 min, briefly sonicated in toluene for 2 min, rinsed with ethanol and water and dried under a stream of nitrogen. This process is applied to all APTES functionalization of the used substrates.

Preparation of graphite oxide

3 g of graphite and 1 g of sodium nitrate were added in 46 mL of sulfuric acid and stirred in an ice-bath. Then, 6 g of potassium permanganate was gradually added to the mixture with stirring and maintained below 20 °C. After addition, the temperature of the graphite slurry was raised to 35 °C and the mixture was stirred for an hour. 40 mL of water was added to the mixture, stirred for 30 min and 100 mL of water was added to the mixture at 0°C to prevent rapid boiling because this process causes rapid boiling of the mixture. Finally, 6 mL of hydrogen peroxide (30 %) was slowly added to the mixture with color change to bright yellow. The final mixture was filtered with filter paper (Number 3, Whatman) and washed with copious water until the filtrate was neutralized. The filtered cake was dried under vacuum for 48 h. The prepared graphite oxide powder was analyzed by FT-IR spectroscopy with a KBr pellet method.

Preparation of MWCNT-NH₂

MWCNT (60 mg) were sonicated in 40 mL of a mixture of HNO₃ and H₂SO₄ (1:3) for 10 h at 60 °C, filtered through an anodic alumina membrane (200 nm pore size) and thoroughly washed with water until the filtrate was neutralized. The filtered cake was dried under vacuum for 3 days. 20 mg of the oxidized MWCNT was dispersed in 20 mL of thionyl chloride containing 1 mL of anhydrous DMF

by sonication for 1 h. The suspension was refluxed for 24 h at 70 °C to activate the carboxylic acid groups on the surface of MWCNT to acid chlorides. The acid chloride-activated MWCNT was collected by rotary-evaporation and the resulting powder was dispersed in 20 mL of ethylenediamine by sonication for 1h. The suspension was refluxed at 125 °C for 5 days with stirring. Finally, the aminated-MWCNT was collected and purified by filtration through an anodic alumina membrane (200 nm pore size), washed with ethanol and water. The resulting aminated-MWCNT was dried under vacuum for 3 days.

Supporting figure

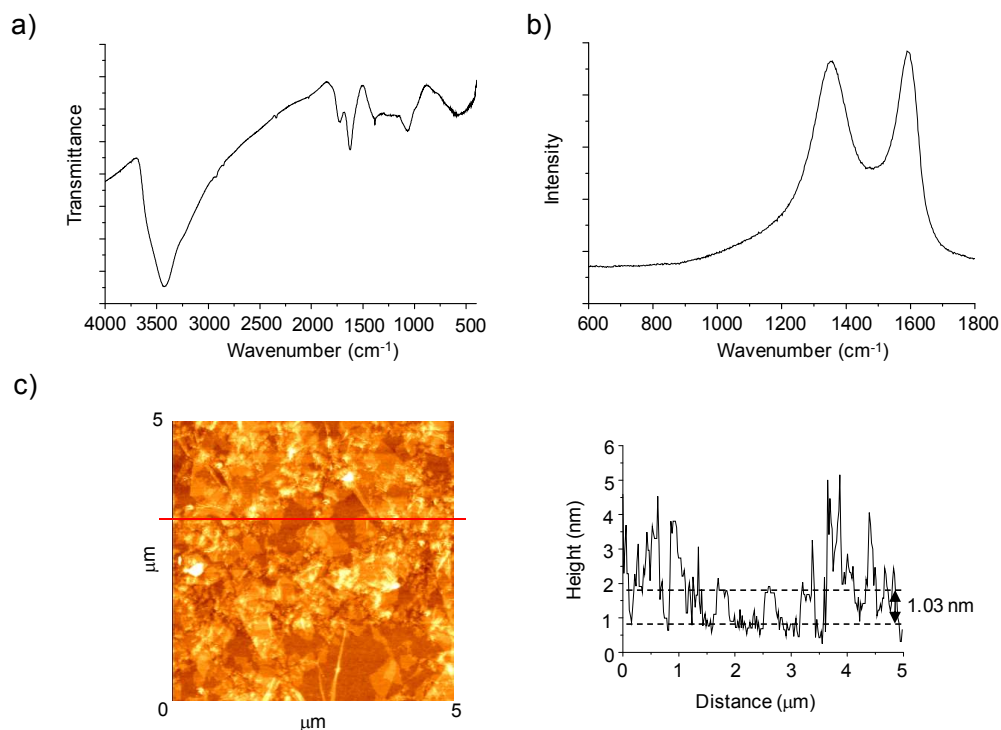


Figure S1. a) The FT-IR spectrum of graphite oxide showed several characteristic oxygen-containing functional groups such as 1079 cm⁻¹ from C-O stretching, 1400 cm⁻¹ from O-H deformation, 1627 cm⁻¹ from C=C skeletal vibrations of the oxidized graphitic domain, 1716 cm⁻¹ from C=O stretching and 3415 cm⁻¹ from O-H vibrations. b) The Raman spectrum of graphite oxide also confirmed the successful oxidation of graphite by appearing the D-peak around 1356 cm⁻¹. The single layer exfoliation of graphite oxide in water was examined by AFM analysis. The thickness of GO sheets was about 1.03 nm corresponding to a single layered GO sheet. The GO films showed high surface coverage.

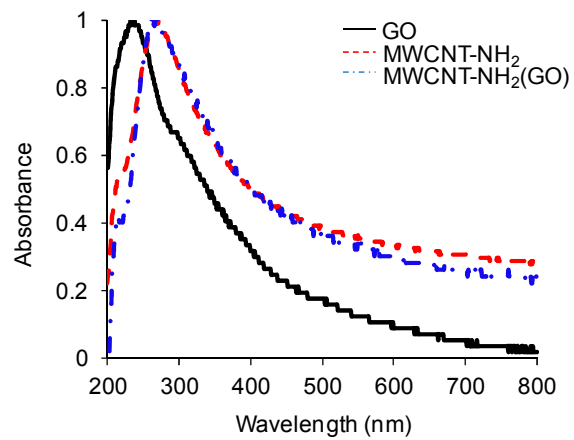


Figure S2. The UV-vis spectra of GO, MWCNT-NH₂ and MWCNT-NH₂(GO) films on quartz substrates. The MWCNT-NH₂ and MWCNT-NH₂(GO) films have high absorption capacity compared to GO films at 355 nm wavelength corresponding to the excitation wavelength of laser equipped in mass spectrometer.

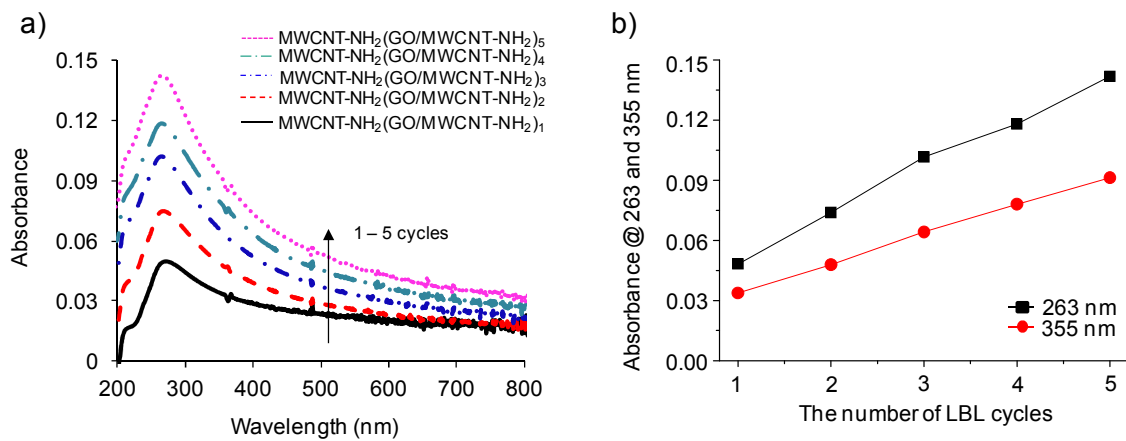


Figure S3. a) The UV-vis spectra and b) absorbance at 263 and 355 nm of MWCNT-NH₂(GO/MWCNT-NH₂)_n multilayer on quartz substrates. The absorbance at 263 and 355 nm was gradually increased with each LBL assembly cycle of GO sheets and MWCNT-NH₂.

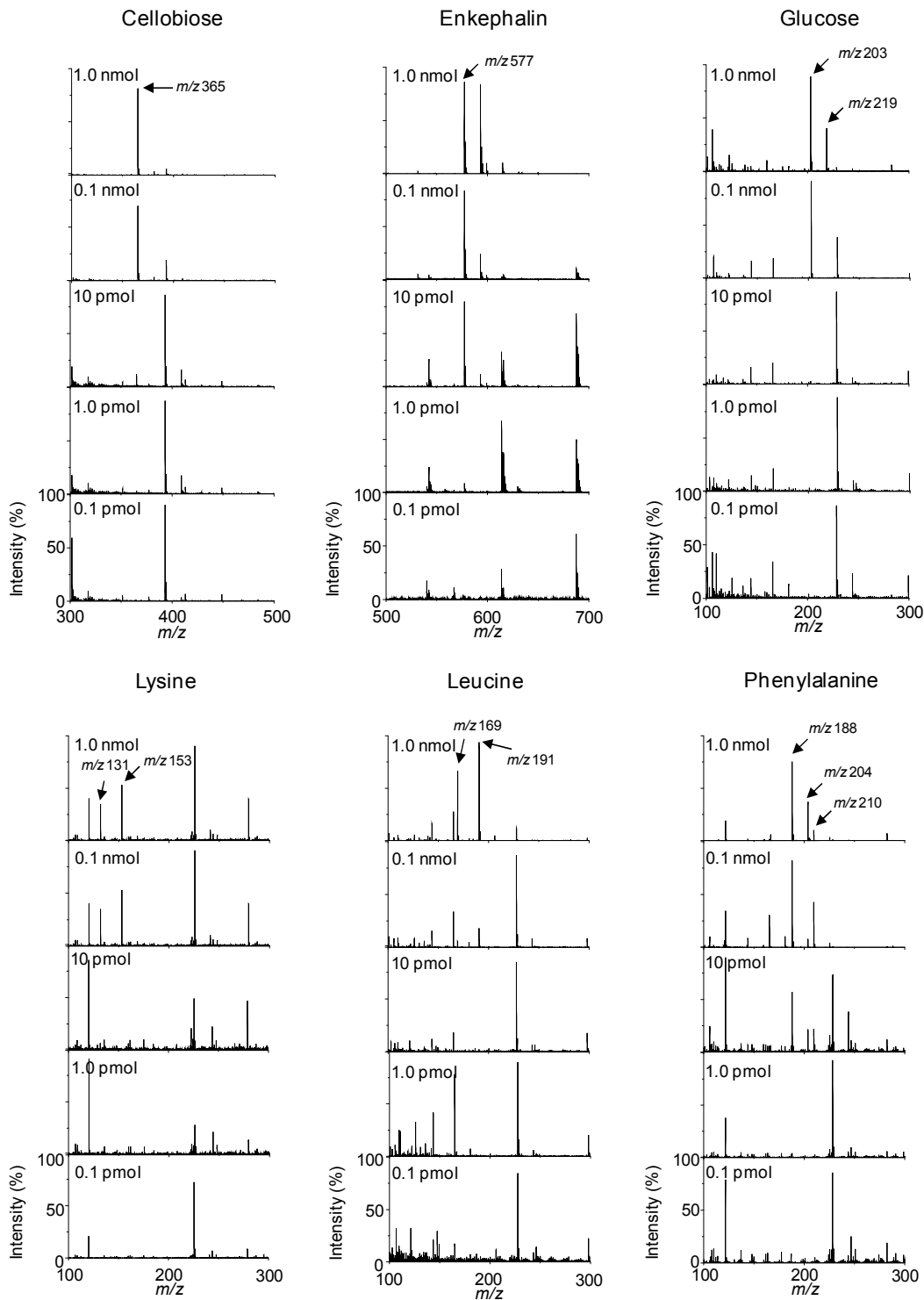


Figure S4. Mass spectra of various small molecules dissolved in water with serial dilution obtained on the MWCNT-NH₂(GO/MWCNT-NH₂)₅ multilayer-coated substrates.

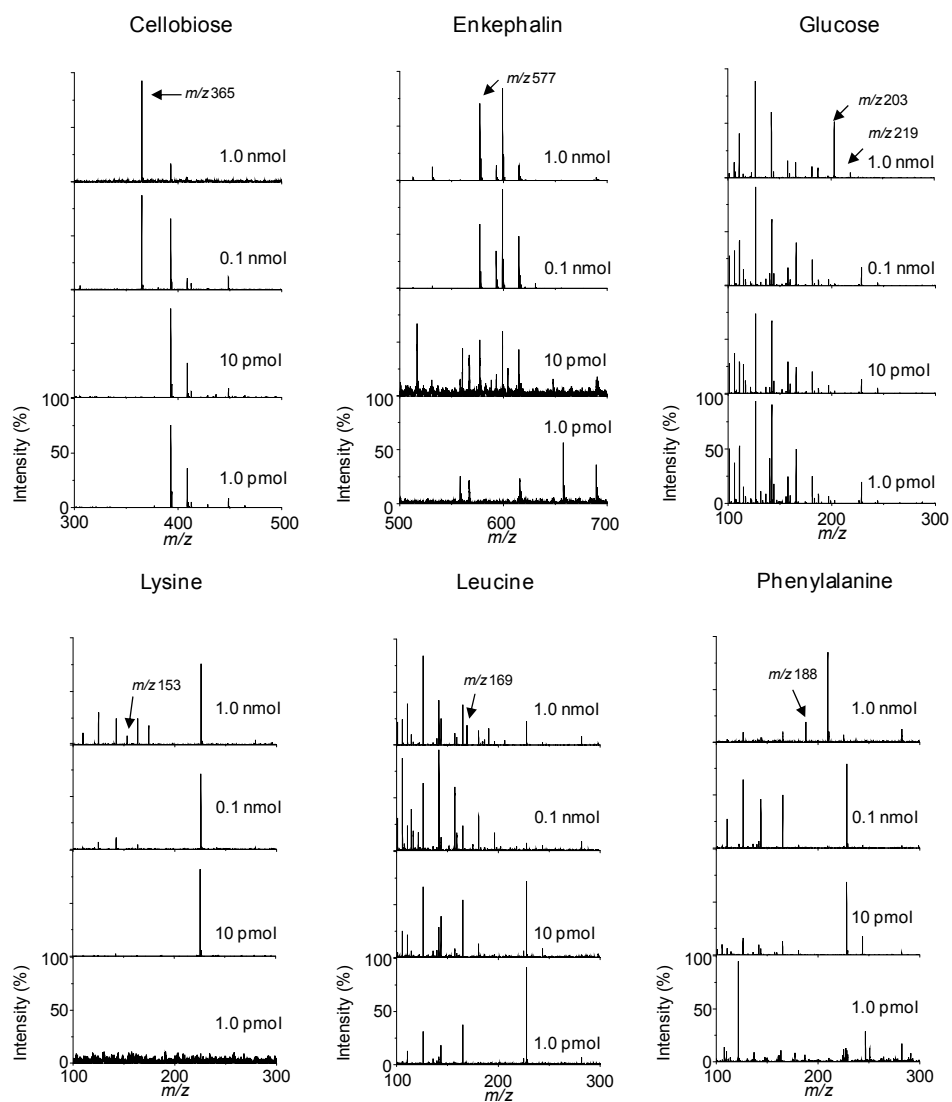


Figure S5. Mass spectra of various small molecules dissolved in PBS buffer with serial dilution obtained on the MWCNT-NH₂(GO/MWCNT-NH₂)₅ multilayer-coated substrates.

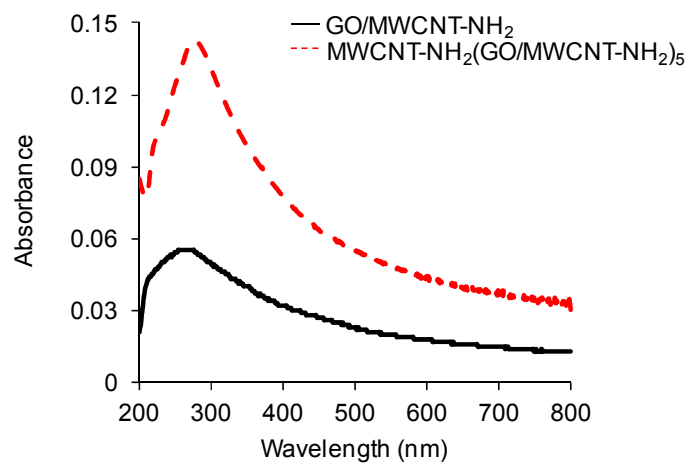


Figure S6. The UV-vis spectra of GO/MWCNT-NH₂ and MWCNT-NH₂(GO/MWCNT-NH₂)₅ multilayer-coated on quartz substrates. The absorbance at 355 nm wavelength was high on the MWCNT-NH₂(GO/MWCNT-NH₂)₅ multilayer compared to GO/MWCNT-NH₂ films. The high absorbance at 355 nm results in high absorption capacity of laser energy from mass spectrometer.