SUPPORTING INFORMATION

for

3D printing of graphene-doped target for "matrix-free" laser desorption/ionization mass spectrometry

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Contents

1. Experimental Section

Chemicals and materials

The 3D printable feedstock used in this study was Formlabs Photopolymer Clear Resin (type: FLGPCL04; Somerville, MA, USA). Single-layer graphene powder (lateral size 0.5-2 μm and layer thickness ~0.8 nm) was bought from XFNANO Co. (Nanjing, China). Ethanol (99.7%) was from Sinopharm Chemical Reagent Co. (Shanghai, China). Perfluorooctanesulfonate (PFOS), hexadecyldimethylbenzylammonium chloride (HDBAC), cetyltrimethylammonium bromide (CTAB), and α-cyano-4-hydroxycinnamic acid (CHCA) were purchased from Sigma (St. Louis, MO, USA). Tetrabromobisphenol A (TBBPA) was from TCI (Tokyo, Japan). 2,2',4,4'-Tetrabromodiphenyl ether (BDE-47) was from Accustandard (New Haven, CT, USA). Pentachlorophenol (PCP) was from Dr. Ehrenstorfer (Augsburg, Germany). The polypeptide Asn-Gly-Ser-Thr-Ile-Val-Asp-Gln-Arg-Leu-Gly-Ser-Glu-Leu-Gly was synthesized by GL Biochem. (Shanghai, China). The ultrapure water was made by Millipore Milli-Q system (Billerica, MA, USA). HPLC grade dichloromethane (DCM) and acetone were from J. T. Baker (Phillipsburg, NJ, USA). All reagents were of analytical grade unless otherwise noted.

3D Printing of MALDI target

The 3D printable graphene-doped resins were prepared by mixing graphene power with a commercial photocuring clear resin. The graphene (0.1, 0.2, 0.5, 1, and 2 wt‰) was added to approximately 100 mL of resin in a glass bottle, and then the mixture was stirred vigorously until graphene was homogenously dispersed. Prior to printing, the resin was ultrasonicated for 10 min and stirred again.

The 3D model of the MALDI target was designed by SolidWorks 2014 (Dassault Systèmes SE, France) to accord with the commercial stainless steel MALDI target (see Figure S1) and adapt to the steel MTP NALDI Adapter (Bruker Daltonics Inc.). The digital model was printed out by a Formlabs Form 2 printer equipped with a 405 nm violet laser with a power of 250 mW using both original clear resin and graphene-doped resins. The layer thickness used for printing was 50 μm. After printing, the printed targets were immersed in ethanol and mildly agitated shortly to remove unreacted resin. Post-curing under UV light was used to strengthen the

mechanical properties of the targets.

Characterization of printed targets

Scanning electron microscopy (SEM) images were obtained using Hitachi SU8010 and SU-8020 scanning electron microscopes (Tokyo, Japan). XPS spectra were obtained on an Escalab 250Xi X-ray photoelectron spectrometer (Thermo Scientific, MA, USA) with Al Kα X-ray radiation as an X-ray source excitation. UV-visible absorption spectra were collected on a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer (Kyoto, Japan). FT-IR spectra were collected by a Thermo Scientific Nicolet 6700 FT/IR Fourier transform infrared spectrometer after pressing with KBr to transparent disks. Raman spectra were obtained on a Renishaw Invia Raman microscope (New Mills, UK) with excitation wavelength 633 nm, 10× objective, laser power 0.1 mW, and exposure time 10 s.

MALDI-TOF MS

MALDI-TOF MS analysis was performed on a Bruker Daltonics Autoflex III Smartbean MALDI-TOF mass spectrometer in reflector mode controlled by a FlexControl software. A 355 nm Nd:YAG laser with a frequency of 200 Hz was used. The spectra were recorded by summing 200 laser shots. The laser power was set to 52% and 51% in negative and positive ion mode, respectively. The 2 μL of sample solution was dropped to the MALDI target followed by air-drying. The data processing was performed by a FlexAnalysis software.

2. Supporting tables

Table S1. Parameters of model analytes used in this study.

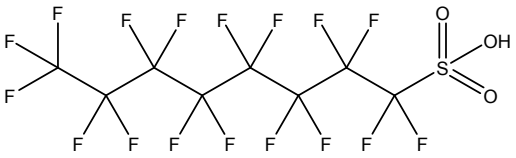
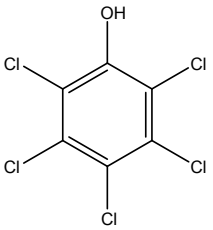
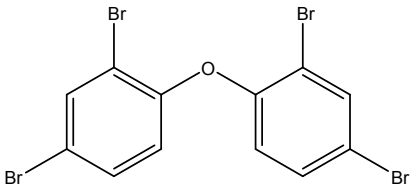
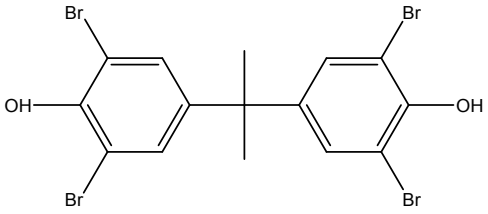
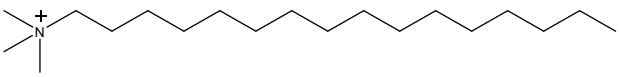
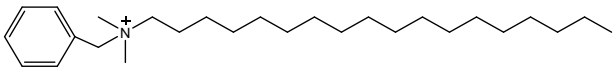
Compound	M_w	Feature peak	Chemical structure
PFOS	500	$[M-H]^-$: 498.5	
PCP	266.3	$[M-H]^-$: 265.4	
BDE-47	485.8	$[M-C_6H_3Br_2]^-$: 250.3	
TBBPA	543.9	$[M-H]^-$: 542.4	
CTAB	364.5	$[M-Br]^+$: 285.2	
HDBAC	396.1	$[M-Cl]^+$: 361.3	

Table S2. Comparison of the reproducibility on a 3DPGDT with a conventional target.

Compound	3D printed target		Conventional target[a]	
	RSD1[b]	RSD2[c]	RSD1[b]	RSD2[c]
BDE-47	35.7%	39.4%	55.2%	49.8%
PCP	21.1%	22.8%	51.8%	57.0%
PFOS	24.9%	21.2%	40.7%	54.6%
TBBPA	26.1%	27.6%	53.9%	36.6%
CTAB	29.2%	19.9%	45.9%	53.7%
HDBAC	39.2%	42.2%	62.9%	59.3%

[a] The data were obtained with a commercial target using graphene as a matrix from Ref. 1.[1]

[b] RSD1: shot-to-shot RSDs measured based on 20 shots at different locations on the matrix (n = 20).

[c] RSD2: sample-to-sample RSDs measured based on 15 samples in different batches (n = 15).

Table S3. Effect of graphene doping concentration on the reproducibility on the 3DPGDT.

Compound	0.1 wt‰ graphene		0.2 wt‰ graphene		0.5 wt‰ graphene		2 wt‰ graphene	
	Shot-to-shot RSD[a]	Sample-to-sample RSD[b]	Shot-to-shot RSD[a]	Sample-to-sample RSD[b]	Shot-to-shot RSD[a]	Sample-to-sample RSD[b]	Shot-to-shot RSD[a]	Sample-to-sample RSD[b]
BDE-47	64.0%	66.3%	47.2%	42.3%	45.9%	51.9%	39.2%	35.8%
PCP	56.2%	48.7%	47.4%	45.9%	49.0%	58.3%	30.9%	27.2%
PFOS	28.5%	49.5%	37.8%	33.8%	32.8%	27.6%	34.4%	52.0%
TBBPA	35.9%	38.9%	21.1%	34.7%	32.2%	40.5%	37.9%	34.0%
CTAB	53.4%	37.3%	53.9%	57.2%	41.1%	44.6%	29.8%	25.2%
HDBAC	37.2%	59.1%	48.2%	49.0%	26.7%	35.8%	30.2%	25.9%

[a] The shot-to-shot RSDs were measured based on 20 shots at different locations on the matrix (n = 20).

[b] The sample-to-sample RSDs were measured based on 15 samples in different batches (n = 15).

3. Supporting figures

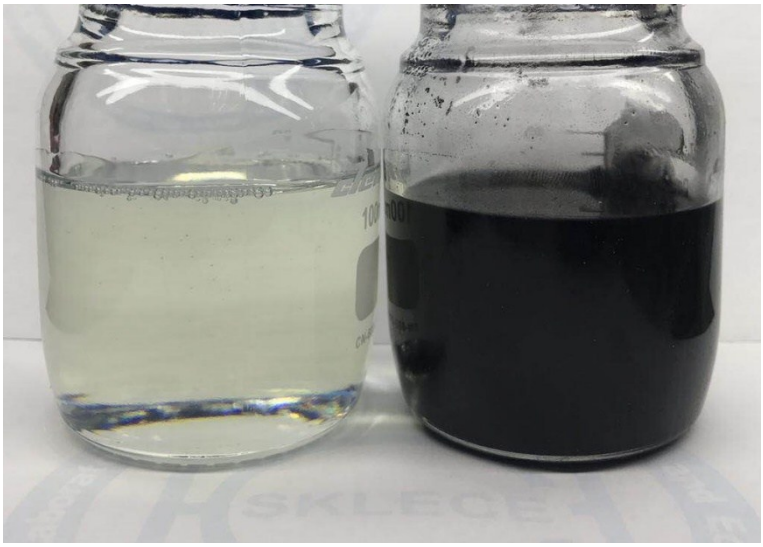


Figure S1. Digital photos of undoped clear resin (left) and graphene-doped resin (right). After doping with graphene, the color of the resin turned from colorless into black. The doped resin could keep stable for long term without visible aggregates or precipitates.

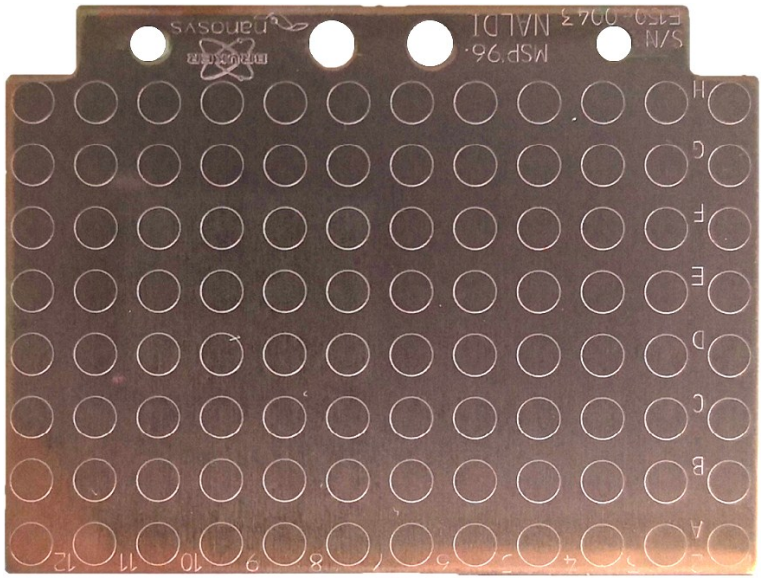


Figure S2. Digital photo of a one-off commercial stainless steel MALDI target (Bruker Daltonics MTP target frame III). The 3D printed graphene-doped MALDI targets adopted the same configuration as the commercial target (as shown in Figure 1).

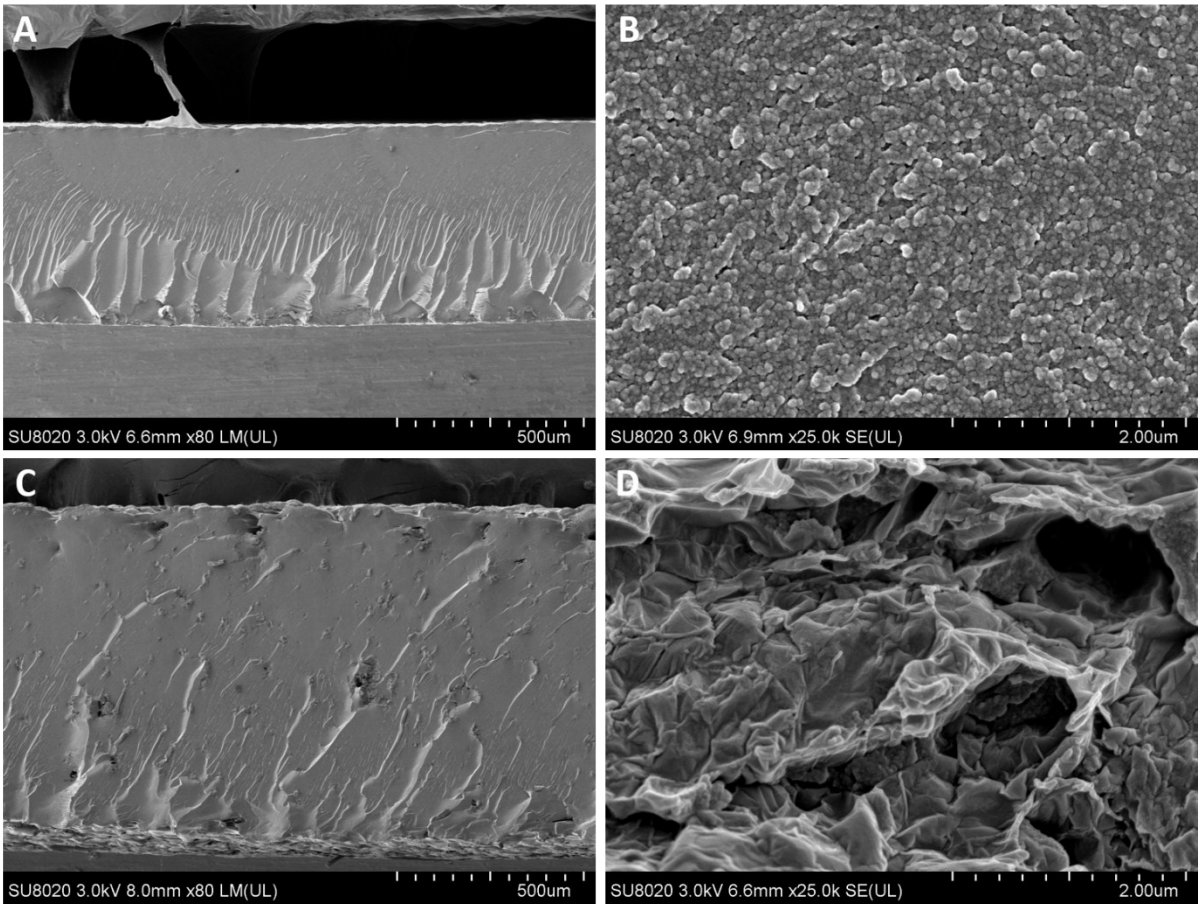


Figure S3. SEM characterization of the cross-sections of the undoped (**A**,**B**) and graphene-doped 3D printed targets (**C**,**D**) at different resolutions. From **A**, the cross-section of the undoped target was featureless and the high-resolution image (**B**) shows that it consisted of uniform resin particles. While for the graphene-doped target (**C**), the graphene sheets could be observed in the whole target with some clustering of graphene. The high-resolution image (**D**) shows that the graphene in the target maintained the wrinkled nanosheet structure.

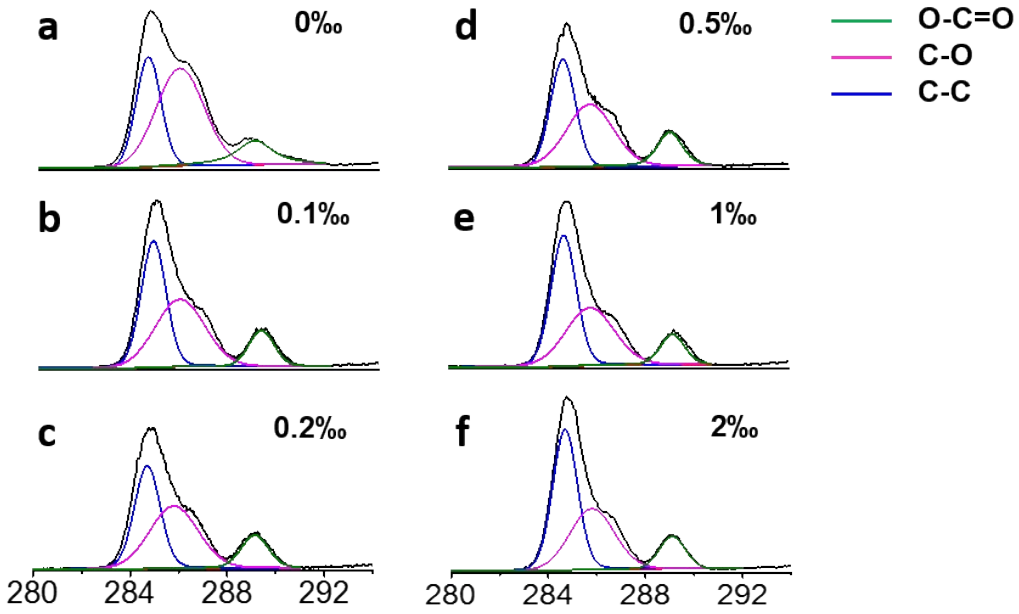


Figure S4. C1s XPS spectra of 3D printed MALDI targets by using resin containing 0 (**a**), 0.1 wt‰ (**b**), 0.2 wt‰ (**c**), 0.5 wt‰ (**d**), 1 wt‰ (**e**), and 2 wt‰ graphene (**f**). The peaks at 284.5, 285.4, and 288.9 eV were assigned to C-C, C-O, and O-C=O bonds, respectively. The ratio of C-C to C-O bonds gradually increased with the increase of graphene concentration, and the intensity of C-C bond of 2 wt‰ graphene target was stronger than that of other targets, indicating the successful doping of graphene in the targets.

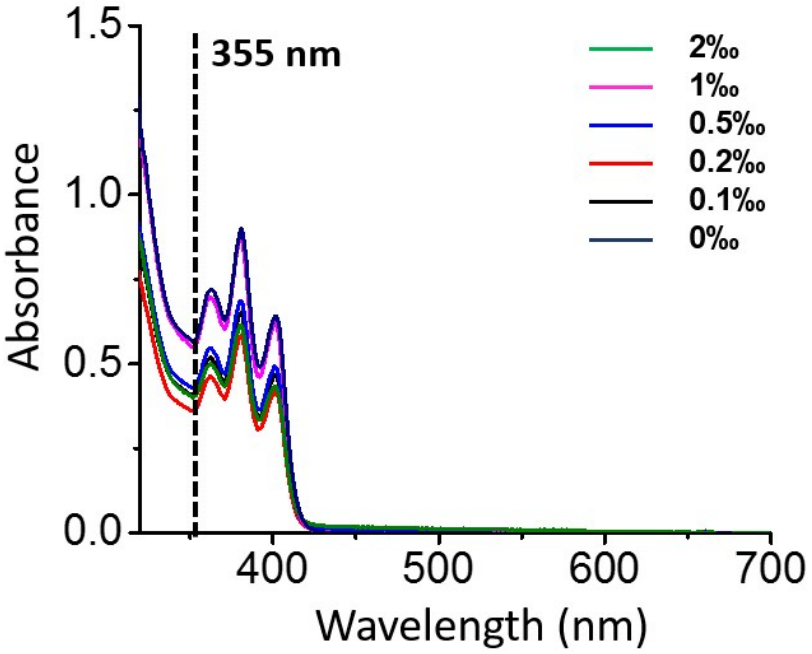


Figure S5. UV-visible absorption spectra of 3D printing resin doped with 0, 0.1 wt‰, 0.2 wt‰, 0.5 wt‰, 1 wt‰, and 2 wt‰ graphene. It can be seen that all materials have optical absorption at 355 nm (the wavelength of laser used in MALDI-TOF MS). The concentration of graphene did not greatly affect the optical absorption, because the original resin also had a strong absorption at that wavelength and the doping concentration was relatively low.

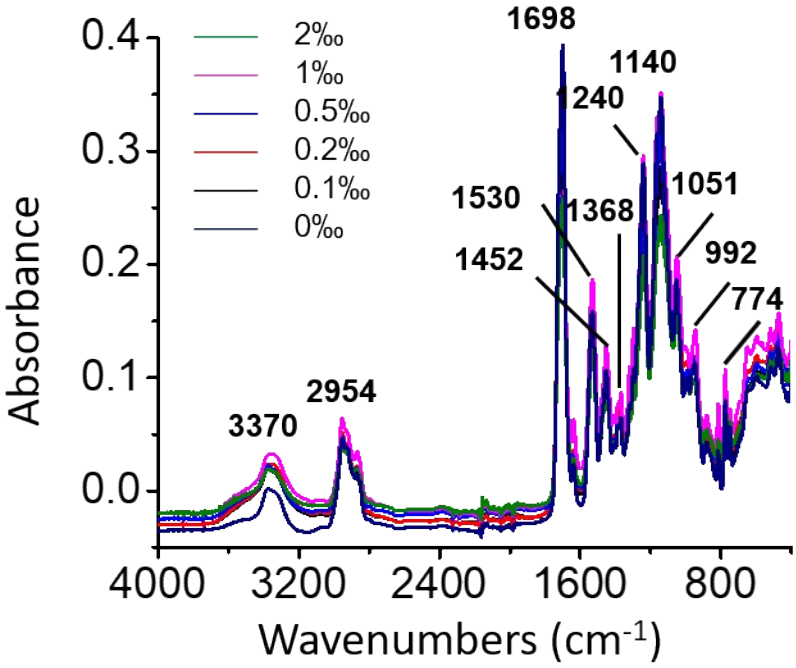


Figure S6. FT-IR absorption spectra of 3D printed MALDI targets printed by resin doped with 0, 0.1 wt‰, 0.2 wt‰, 0.5 wt‰, 1 wt‰, and 2 wt‰ graphene. They exhibited a broad peak at 3370 cm^{-1}, which was assigned to the O-H stretching vibration. The peaks at 1530, 992, and 774 cm^{-1} were assigned to the skeletal ring vibrations and the external bending of C-H bonds. The peaks at 2954, 1452, and 1368 cm^{-1} were ascribed to the asymmetric C-H stretching vibration, the asymmetric C-H bending vibration, and the symmetric C-H bending vibration, respectively. The peaks of oxygen functionalities were mainly located at 1698, 1240, 1140, and 1051 cm^{-1}, which were ascribed to the C=O stretching vibration, the asymmetric C-O-C stretching vibration, and the symmetric C-O-C stretching vibration.

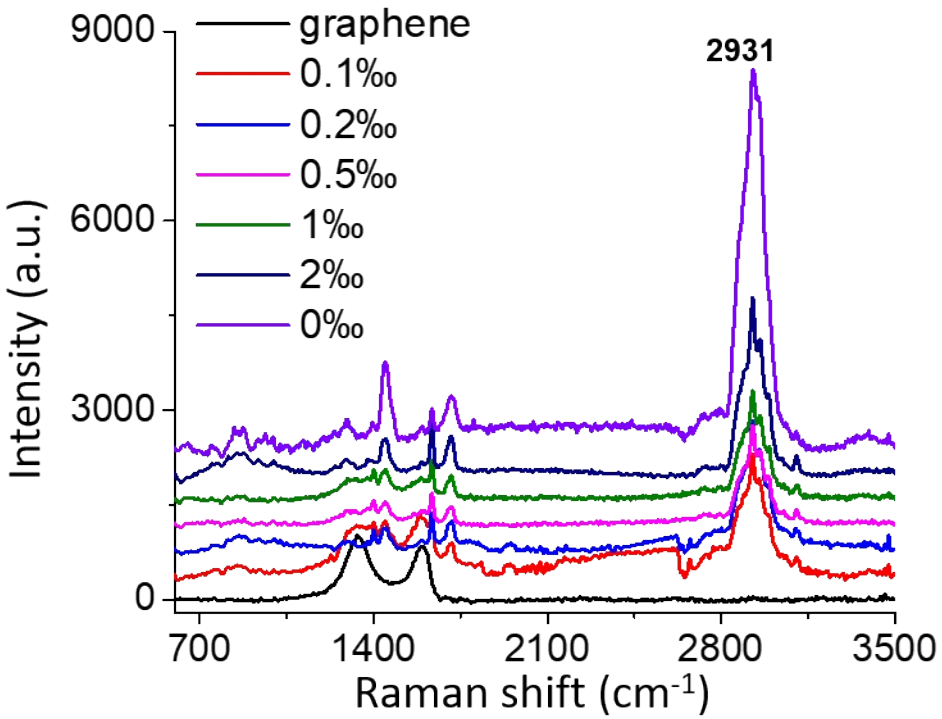


Figure S7. Raman characterization of MALDI targets printed by resin doped with 0, 0.1 wt‰, 0.2 wt‰, 0.5 wt‰, 1 wt‰, and 2 wt‰ graphene. An intense band at 2931 cm^{-1} was assigned to the asymmetric C-H stretching. The broad bands of 1448 cm^{-1}, 1715 cm^{-1}, and a sharp line of 1635 cm^{-1} were assigned to the H-C-H bending, asymmetric O=C-O stretching, and C=C stretching, respectively. The characteristic Raman bands of graphene were obtained at 1335 and 1596 cm^{-1}, which were ascribed to the defects and disordered structures of the sp^2 domains and E_{2g} C-C stretching, respectively.[2, 3] This pair of bands were obtained with all 3D printed targets, suggesting that graphene was successfully doped in the targets.

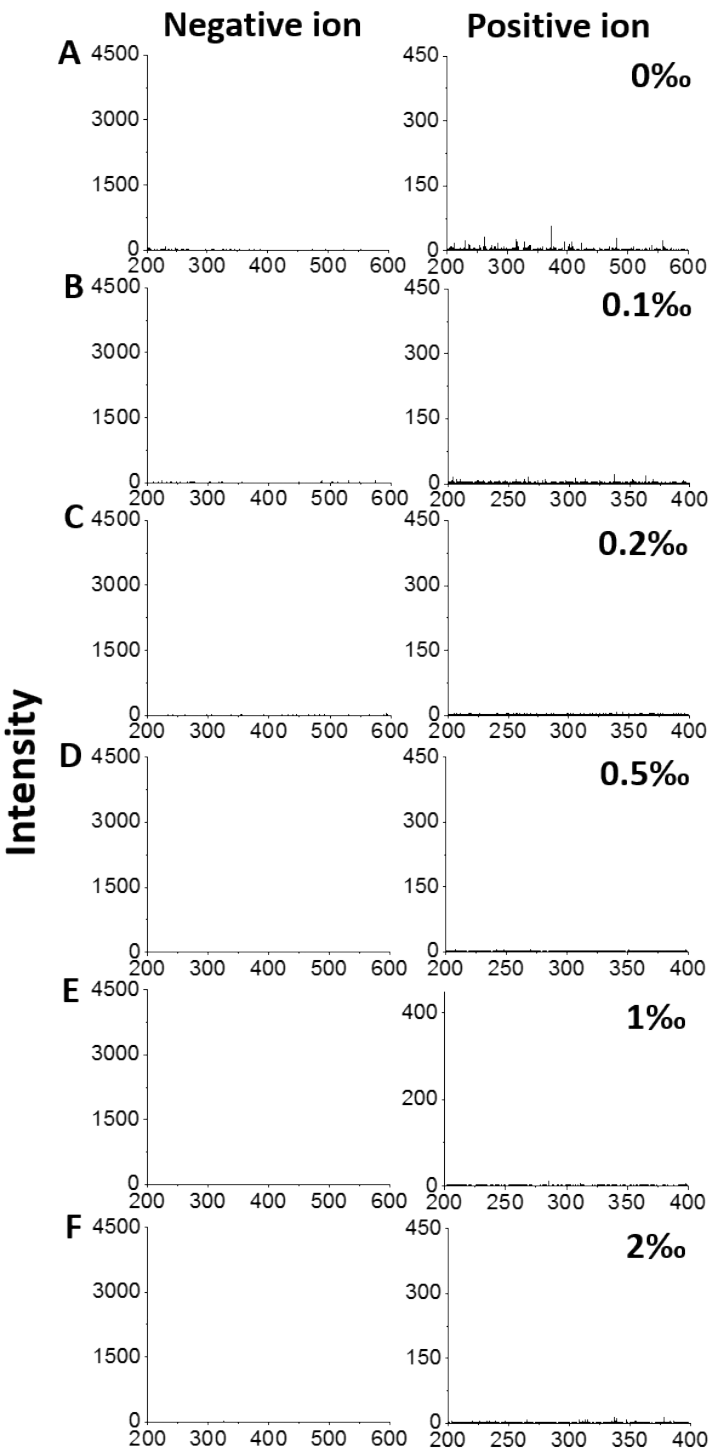


Figure S8. The negative and positive ion mode mass spectra for blank control on 3D printed graphene-doped MALDI targets. Graphene concentration: 0 wt‰ (**A**), 0.1 wt‰ (**B**), 0.2 wt‰ (**C**), 0.5 wt‰ (**D**), 1 wt‰ (**E**), and 2 wt‰ (**F**).

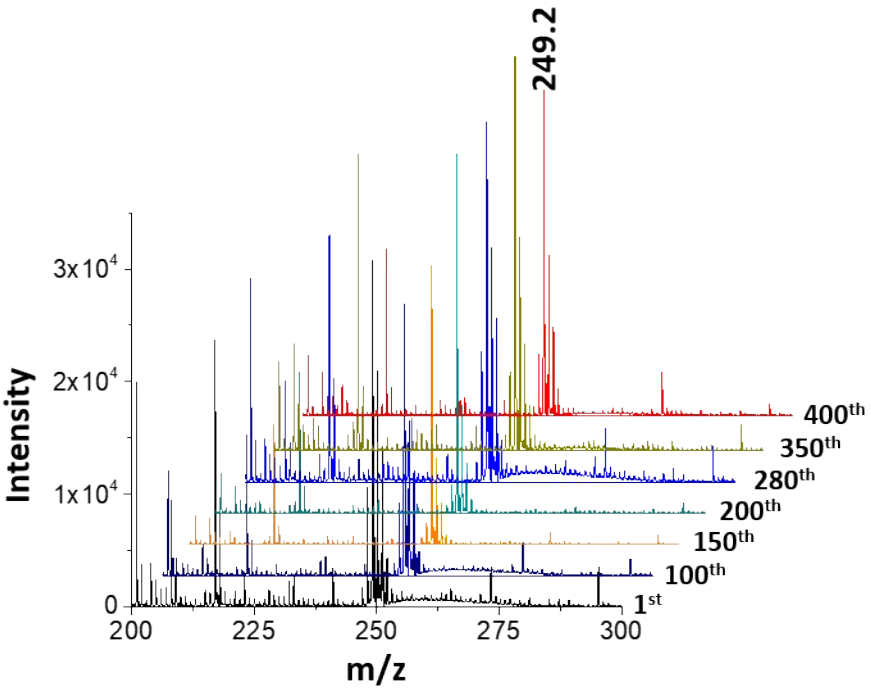


Figure S9. Reusability test of the 3D printed target. Bisphenol S (BPS) was used as a model analyte. Analyte concentration: 1000 µg/mL. After the sample was added onto the target, the MS spectra of the analyte were repeatedly measured at the same spot for successive 400 laser shots. After each 100 shots, the sample was re-added to the same spot.

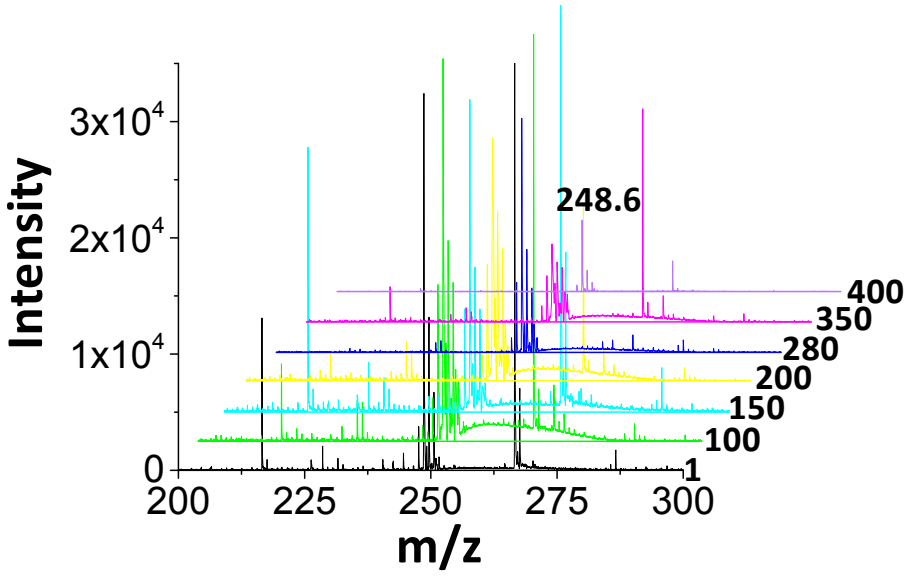


Figure S10. Reusability test of graphene matrix on a conventional MALDI target. The sample solution was mixed with graphene matrix, and then the mass spectra of successive 400 laser shots at one spot were recorded. BPS was used as a model analyte. Analyte concentration: 1000 μg/mL. After each 100 shots, the sample was re-added to the same spot without replenishing the matrix. It can be seen that after 200 laser shots the intensity of the MS signals decreased by 30%. After 350 laser shots, only 20% intensity remained due to the consumption of the matrix.

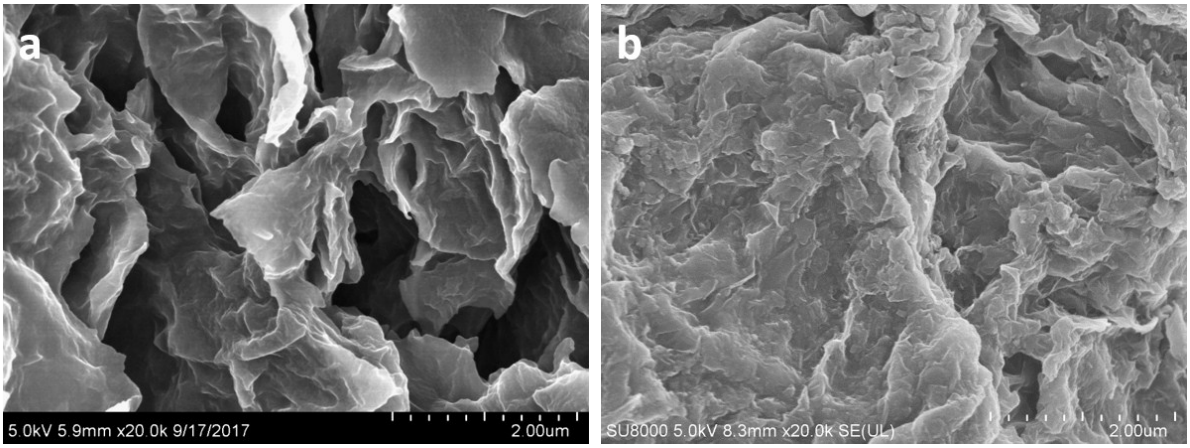


Figure S11. SEM characterization of 3D printed MALDI target before (**a**) and after (**b**) 400 successive laser shots. Graphene concentration: 1 wt‰. It can be seen that after 400 laser shots, some graphene sheets on the target surface were ablated by the laser. However, because graphene was doped in the whole target, the target still had much graphene structure on the surface, which maintained the high performance in MALDI.

References for SI

1. X. Huang, Q. Liu, J. J. Fu, Z. Nie, K. Gao and G. B. Jiang, *Anal. Chem.*, 2016, **88**, 4107-4113.
2. X. Chen and B. Chen, *Environ. Sci. Technol.*, 2015, **49**, 6181-6189.
3. J. Wang, Z. Chen and B. Chen, *Environ. Sci. Technol.*, 2014, **48**, 4817-4825.