Supplementary Information

N-doped graphene quantum dots as a novel matrix of high efficacy for the analysis of perfluoroalkyl sulfonates and other small molecules by MALDI-TOF MS

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Supplementary graphs and tables

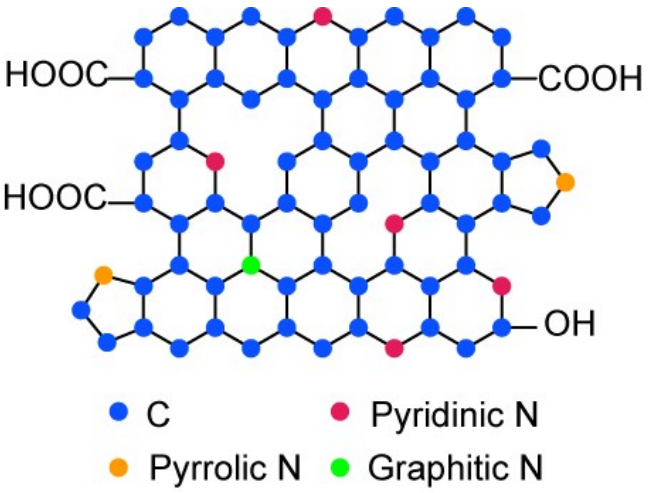

Fig. S1 Possible atomic distribution of a N-GQD (not drawn to scale).

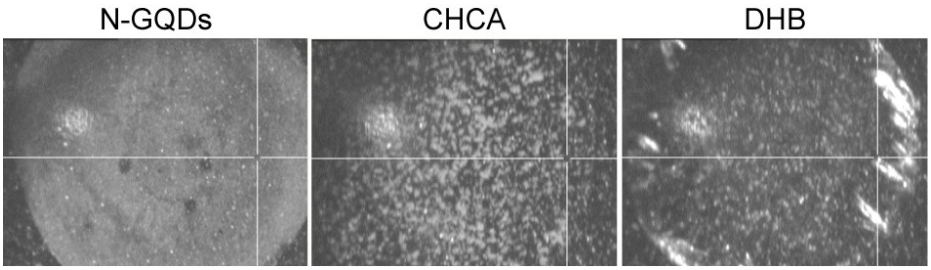

Fig. S2 Photos of N-GQDs, CHCA and DHB with the analyte on MALDI target, taken by the camera equipped inside the MALDI-TOF MS instrument.

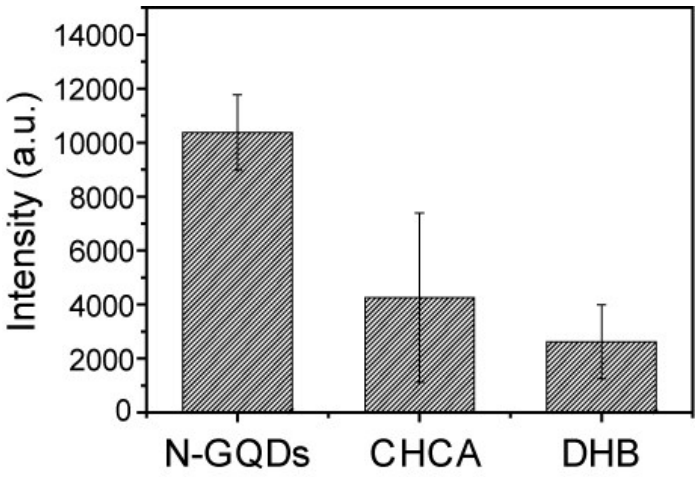

Fig. S3 Average intensities of $[PFOS - H]^-$ at random 30 shot spots with N-GQDs, CHCA and DHB as the matrix.

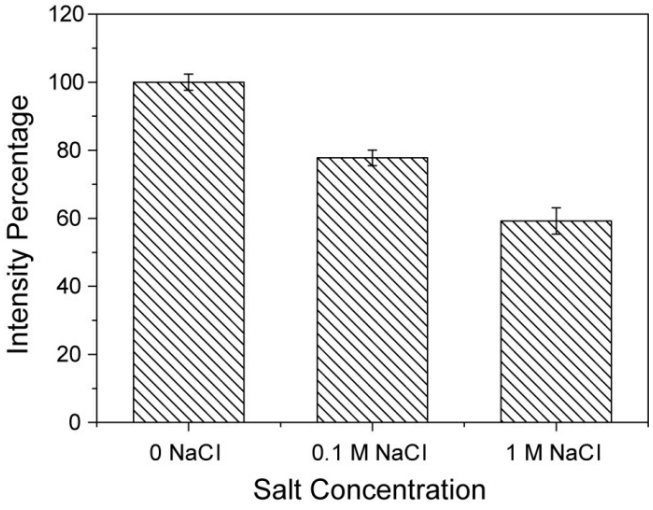

Fig. S4 Intensity changes of PFOS using N-GQDs as the matrix with different salt concentrations

Tolerance of N-GQDs to high concentration salt was assessed with the analysis of a 50 μg/ml PFOS solution containing 0.1 and 1.0 M NaCl and that without salt as the control. The intensities of 30 random shot spots were collected and calculated with the average and RSD. The obtained results displayed that the intensities decreased to about 80% with 0.1 M NaCl and 60% with 1.0 M NaCl as compared to that without salt but the S/N ratios were still far higher than 3. In addition, the RSDs were still small revealing excellent shot-to-shot repeatability even if the concentration of salt was high to 1.0 M. Consequently, it is reasonable to conclude that N-GQDs have good tolerance to high concentration salt as a matrix in MALDI-TOF MS analyses.

Table S1 Intensities and percentages of different forms of nitrogen atoms obtained from the deconvolution of N 1s high-resolution XPS spectra

	N 1s Total	Pyridinic	Pyrollic	Graphitic	Oxidized
Intensity (a.u.)	9529.31	7566.03	1467.86	322	173.41
Proportion (%)	100	79.40	15.40	3.38	1.82

Table S2 Intensities and percentages of different forms and chemical environments of carbon atoms obtained from the deconvolution of C 1s high-resolution XPS spactra

	C 1s Total	C-C	C-OH	C-N	C=O	C(O)-O
Intensity (a.u.)	77177.85	52388.94	7184.77	2661.03	6918.67	8024.45
Proportion (%)	100	67.8808	9.3094	3.4479	8.9646	10.3973

Table S3 Elemental atomic percentages of N-GQDs obtained from XPS survey spectra.

	C 1s	N 1s	O 1s	Total
Proportion (%)	70.98	5.87	23.14	99.99

Table S4 Intensity fold changes of N-GQDs/CHCA, N-GQDs/DHB with the analyses of PFBS, PFHxS and PFOS, respectively.

MS Intensity Fold Change	PFBS	PFHxS	PFOS
N-GQDs/CHCA	5.85	5.31	8.32
N-GQDs/DHB	161.5	45.93	61.06