Supporting Information

The efficient profiling of serum N-linked glycans by a highly porous 3D graphene composite

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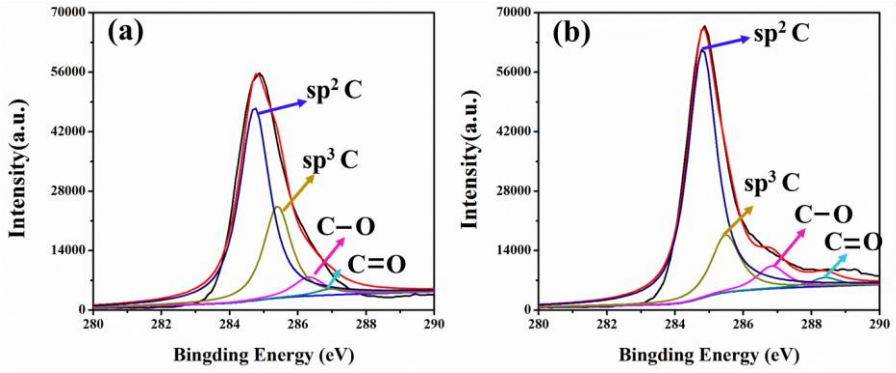


Fig. S1. High-resolution XPS spectra of C1s and its deconvolution for the products: (a) pGO/PF; (b) 3D graphene.

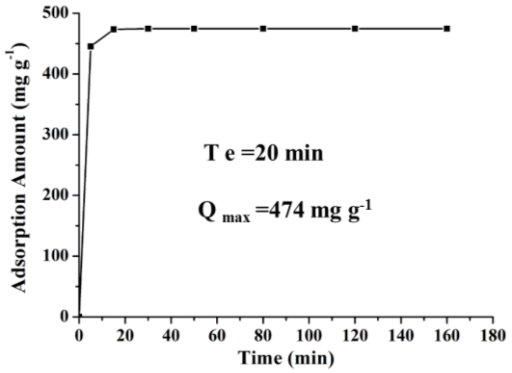


Fig. S2. Kinetic adsorption curve of β-CD on 3D graphene material.

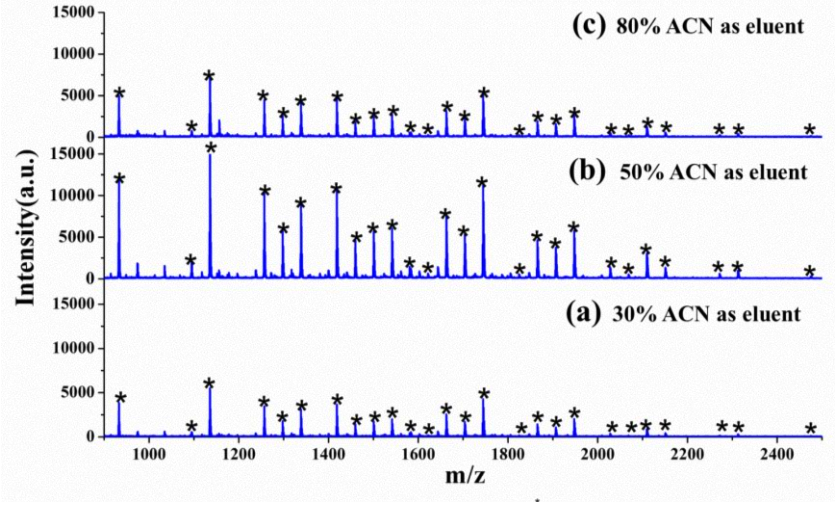


Fig. S3. MALDI-TOF MS analysis of N-linked glycans by using different concentrations of

acetonitrile as eluent: (a) 30% ACN; (b) 50% ACN; (c) 80% ACN. (*, glycans released from ovalbumin).

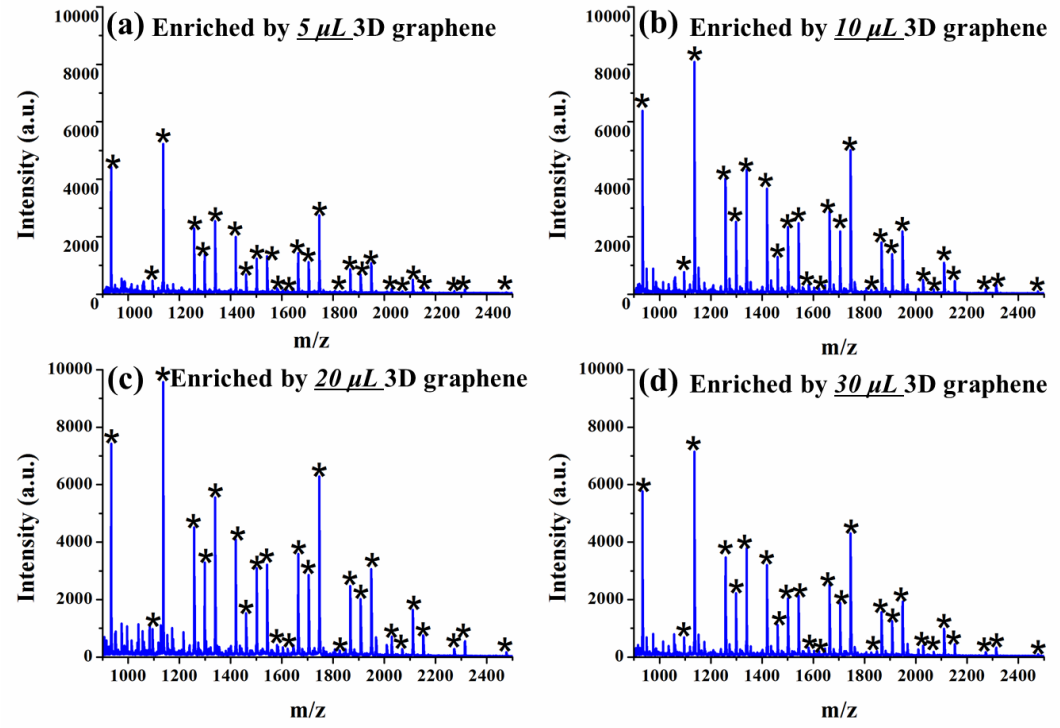


Fig. S4. MALDI-TOF MS analysis of N-linked glycans after the enrichment by (a) 5 μL; (b) 10 μL; (c) 20 μL; (d) 30 μL of 3D graphene material suspension (4 mg mL^{-1}). (*, glycans released from ovalbumin).

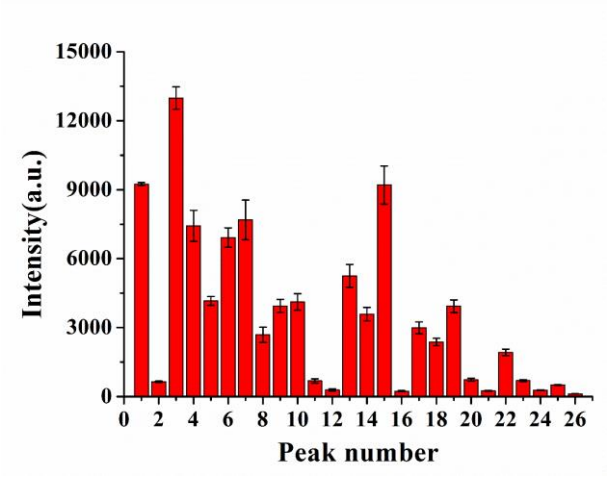


Fig. S5. Average peak intensity of each N-linked glycan identified by 3D graphene enrichment

from OVA digest. The error bars represent the standard deviations of three parallel tests.

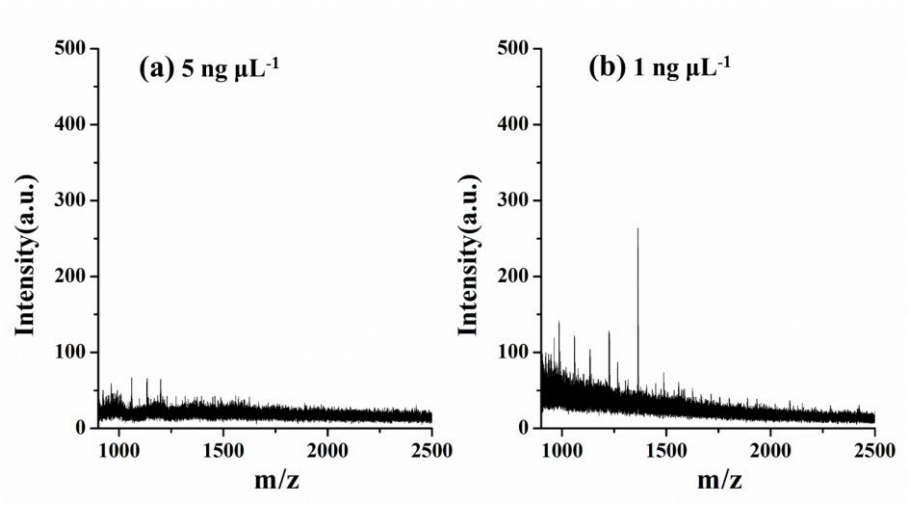


Fig. S6. Direct MALDI-TOF MS analysis of N-linked glycans from OVA digest at the concentrations of 5 ng μL^{-1} and 1 ng μL^{-1}, respectively.

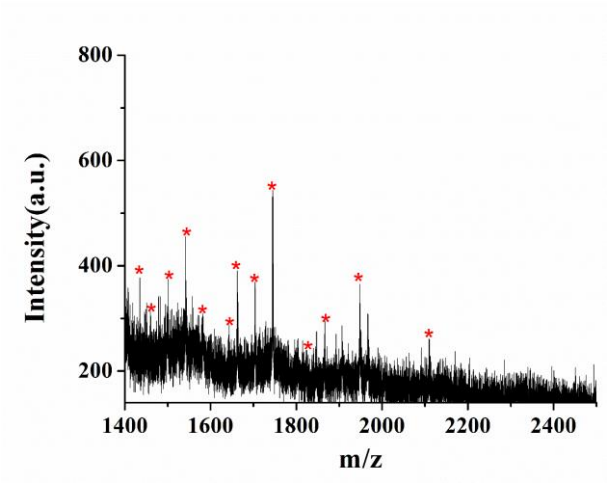


Fig. S7. MALDI-TOF MS analysis of N-linked glycans from OVA digest at the concentration of 0.25 ng μL^{-1} by 3D graphene enrichment. The captured N-glycans were marked with * label.

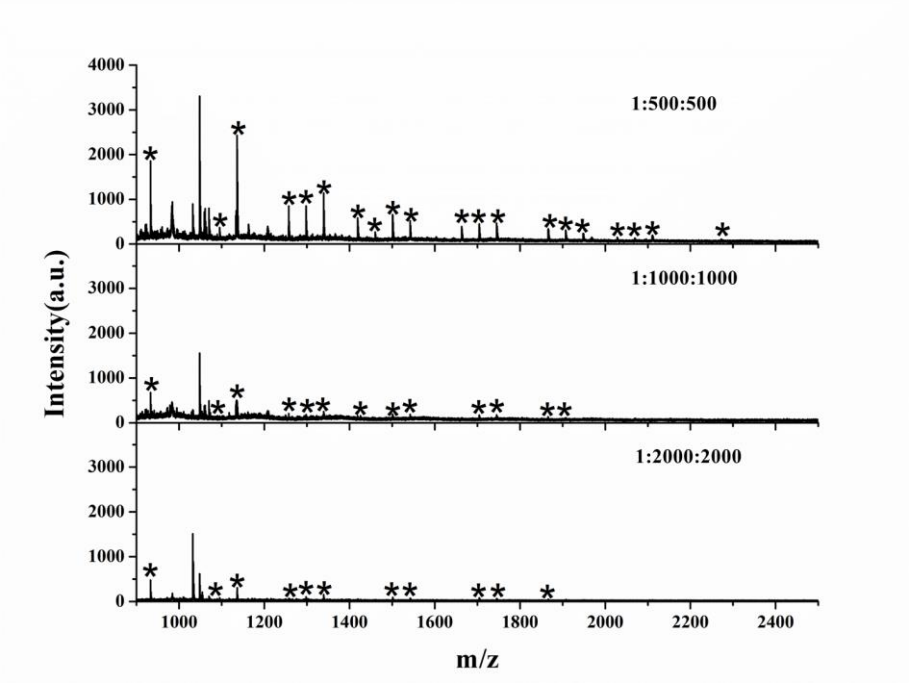
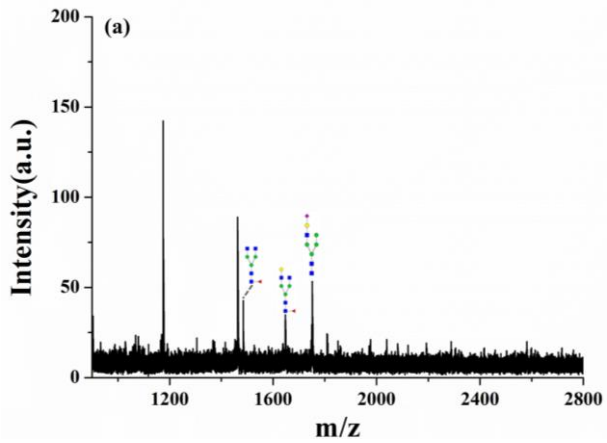


Fig. S8. MALDI-TOF MS analysis of N-linked glycans from a mixture of OVA digest, BSA, and OVA at mass ratio from 1:500:500 to 1:2000:2000 by PGC enrichment. (*, glycans released from OVA digest)



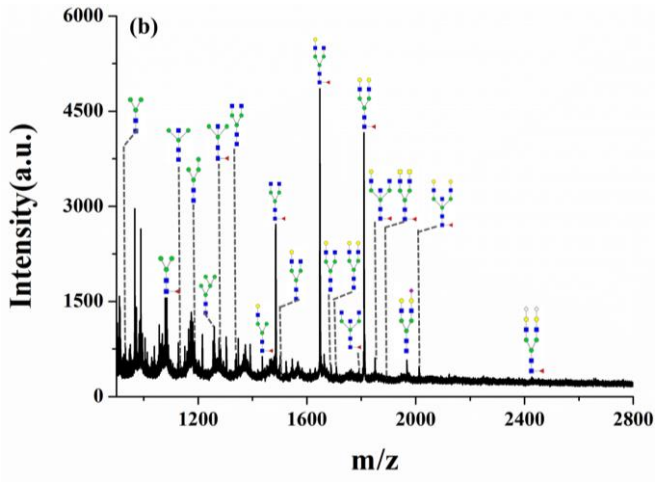


Fig. S9. MALDI-TOF MS analysis of N-linked glycans from human serum digestion, (a) direct analysis, (b) after enrichment with PGC. (The glycan structures were searched by using GlycoWorkbench based on the molecular weight of the oligosaccharide with the mass accuracy of 1.0 Da. Symbols in composition: Hex= Hexose; HexNAc= N-acetyl hexosamine; dHex= Fucose; NeuAc= N-acetylneuramic acid, ●mannose; ●galactose; ◆sialic acid; ◇N-glycolyl sialic acid; ▲fucose; ■N-acetyl glucosamine)

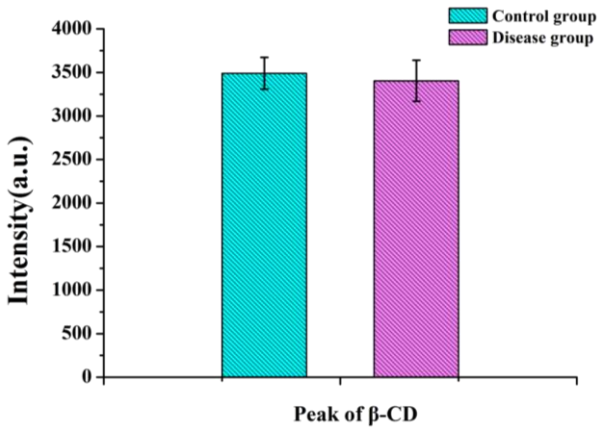
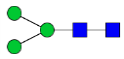
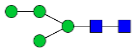
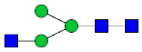
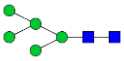
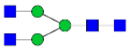
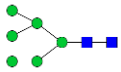
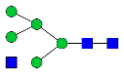
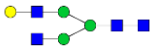
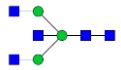
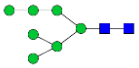
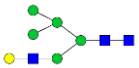
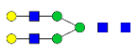
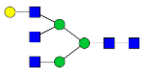


Fig. S10. The average peak intensities of β-CD as an internal standard in the control group and the disease group, respectively. The error bars represent the standard deviations of three parallel detections by MALDI-TOF MS analysis.

Table S1. List of identified 26 N-linked glycans released from ovalbumin enriched by 3D graphene. The glycan structures were searched by using GlycoWorkbench based on the molecular weight of the oligosaccharide with the mass accuracy of 1.0 Da. Symbols in composition: Hex= Hexose; HexNAc= N-Acetyl hexosamine, ● mannose; ○ galactose; ■ N-acetyl glucosamine.

No	M/Z $[M+ Na]^+$	S/N	Structure (M)	Composition
1	933.2	1826.9		$Hex_3HexNAc_2$
2	1095.4	328.8		$Hex_4HexNAc_2$
3	1136.4	2529		$Hex_3HexNAc_3$
4	1257.4	1526.2		$Hex_5HexNAc_2$
5	1298.4	878.4		$Hex_4HexNAc_3$
6	1339.2	1290		$Hex_3HexNAc_4$
7	1419.3	1498		$Hex_6HexNAc_2$
8	1460.4	592		$Hex_5HexNAc_3$
9	1501.3	762.2		$Hex_4HexNAc_4$
10	1542.3	781.6		$Hex_3HexNAc_5$
11	1581.4	165.2		$Hex_7HexNAc_2$
12	1622.1	64.3		$Hex_6HexNAc_3$
13	1663.2	928.5		$Hex_5HexNAc_4$
14	1704.2	698.9		$Hex_4HexNAc_5$

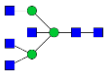
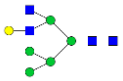
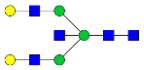
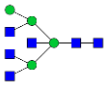
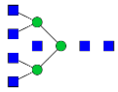
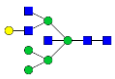
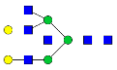
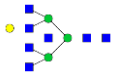
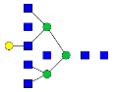
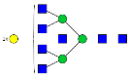
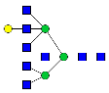
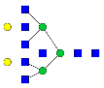
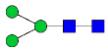
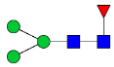
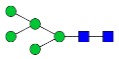
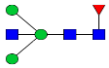
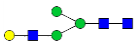
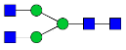
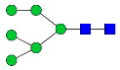
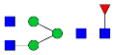
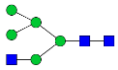
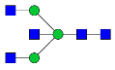
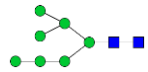
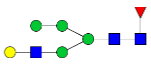
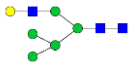
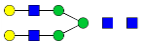
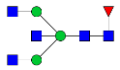
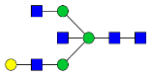
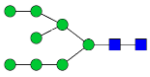
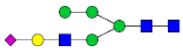
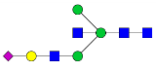
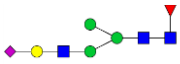
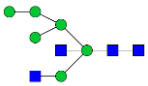
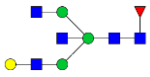
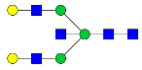
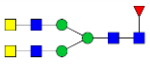
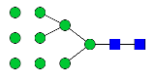
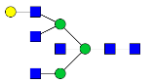
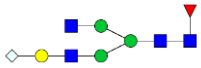
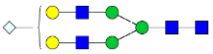
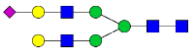
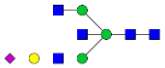
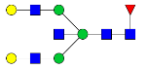
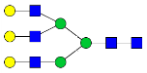
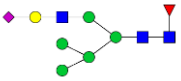
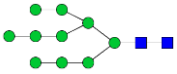
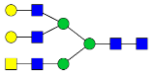
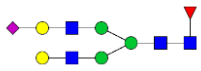
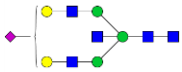
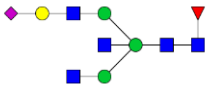
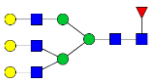
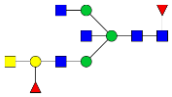
15	1745.2	1546.6		$Hex_3HexNAc_6$
16	1825.1	64.8		$Hex_6HexNAc_4$
17	1866.2	692.5		$Hex_5HexNAc_5$
18	1907.2	539.2		$Hex_4HexNAc_6$
19	1948.2	886.5		$Hex_3HexNAc_7$
20	2028.1	242.6		$Hex_6HexNAc_5$
21	2069.1	90.2		$Hex_5HexNAc_6$
22	2110.1	625.9		$Hex_4HexNAc_7$
23	2151.2	284.2		$Hex_8HexNAc_4$
24	2272.1	159.6		$Hex_4HexNAc_7$
25	2313.2	289.7		$Hex_3HexNAc_8$
26	2475.1	74.9		$Hex_5HexNAc_8$

Table S2. List of the identified 53 N-linked glycans released from human serum enriched by 3D graphene. The glycan structures were searched by using GlycoWorkbench based on the molecular weightof the oligosaccharide with the mass accuracy of 1.0 Da. Symbols in composition: Hex= Hexose; HexNAc= N-Acetyl hexosamine; dHex= Fucose; NeuAc= N-acetylneuramic acid, ● mannose; ○ galactose; ◆ sialic acid; ◇ N-glycolyl sialic acid; ▲ fucose; ■ N-acetyl glucosamine.

No	M/Z	S/N	Structure (M)	Composition (M)
1	933.3 $[M+Na]^+$	46.2		$Hex_3HexNAc_2$
2	1078.9 $[M+Na]^+$	329.9		$Hex_3HexNAc_2dHex_1$
3	1094.9 $[M+Na]^+$	48.2		$Hex_4HexNAc_2$
4	1136.4 $[M+Na]^+$	42.9		$Hex_3HexNAc_3$
5	1241.1 $[M+Na]^+$	12.6		$Hex_4HexNAc_2dHex_1$
6	1257.5 $[M+Na]^+$	221.6		$Hex_5HexNAc_2$
7	1282.3 $[M+Na]^+$	54.1		$Hex_3HexNAc_3dHex_1$
8	1298.3 $[M+Na]^+$	65.9		$Hex_4HexNAc_3$
9	1339.3 $[M+Na]^+$	80.4		$Hex_3HexNAc_4$
10	1419.5 $[M+Na]^+$	304.9		$Hex_6HexNAc_2$
11	1444.4 $[M+Na]^+$	36		$Hex_4HexNAc_3dHex_1$
12	1485.4 $[M+Na]^+$	1123		$Hex_3HexNAc_4dHex_1$
13	1460.3 $[M+Na]^+$	32.4		$Hex_5HexNAc_3$
14	1501.4 $[M+Na]^+$	232.9		$Hex_4HexNAc_4$
15	1542.6 $[M+Na]^+$	46.5		$Hex_3HexNAc_5$

16	1581.6 $[M+Na]^+$	90.4		$Hex_7HexNAc_2$
17	1605.2 $[M+Na]^+$	26.1		$Hex_5HexNAc_3dHex_1$
18	1621.6 $[M+Na]^+$	28.6		$Hex_6HexNAc_3$
19	1647.4 $[M+Na]^+$	1360.7		$Hex_4HexNAc_4dHex_1$
20	1663.4 $[M+Na]^+$	599.1		$Hex_5HexNAc_4$
21	1688.5 $[M+Na]^+$	224.3		$Hex_3HexNAc_5dHex_1$
22	1704.4 $[M+Na]^+$	63.2		$Hex_4HexNAc_5$
23	1743.6 $[M+Na]^+$	136		$Hex_8HexNAc_2$
24	1752.0 $[M+Na]^+$	203.5		$Hex_5HexNAc_3NeuAc_1$
25	1792.8 $[M+Na]^+$	12.2		$Hex_4HexNAc_4NeuAc_1$
26	1809.5 $[M+Na]^+$	907.6		$Hex_5HexNAc_4dHex_1$
27	1816.5 $[M+Na]^+$	54.1		$Hex_4HexNAc_3NeuAc_1$ $dHex_1$
28	1825.5 $[M+Na]^+$	24		$Hex_6HexNAc_4$
29	1850.5 $[M+Na]^+$	312.6		$Hex_4HexNAc_5dHex_1$
30	1866.5 $[M+Na]^+$	42.4		$Hex_5HexNAc_5$
31	1891.8 $[M+Na]^+$	25.3		$Hex_3HexNAc_6dHex_1$

32	1905.7 $[M+Na]^+$	200		$Hex_9HexNAc_2$
33	1909.7 $[M+Na]^+$	104		Hex_4HeNAc_6
34	1953.6 $[M+Na]^+$	10.8		$Hex_4HexNAc_4NeuAc_1$ $dHex_1$
35	1970.5 $[M+Na]^+$	13.3		$Hex_5HexNAc_4NeuAc_1$
36	1976.2 $[M+2Na-H]^+$	429.5		$Hex_5HexNAc_4NeuAc_1$
37	1995.8 $[M+Na]^+$	10.6		$Hex_4HexNAc_5NeuAc_1$
38	2012.6 $[M+Na]^+$	181.1		$Hex_5HexNAc_5dHex_1$
39	2028.6 $[M+Na]^+$	27.7		Hex_6HeNAc_5
40	2056.3 $[M+Na]^+$	34.2		$Hex_6HexNAc_3NeuAc_1$ $dHex_1$
41	2067.1 $[M+Na]^+$	17.4		$Hex_{10}HeNAc_2$
42	2069.8 $[M+Na]^+$	10.4		Hex_5HeNAc_6
43	2122.2 $[M+2Na-H]^+$	199.2		$Hex_5HexNAc_4NeuAc_1$ $dHex_1$
44	2157.2 $[M+Na]^+$	17.4		$Hex_5HexNAc_5NeuAc_1$
45	2162.8 $[M+2Na-H]^+$	11.3		$Hex_4HexNAc_5NeuAc_1$ $dHex_1$
46	2174.8 $[M+Na]^+$	16.5		$Hex_6HexNAc_5dHex_1$
47	2199.7 $[M+Na]^+$	26.6		$Hex_4HexNAc_6dHex_2$

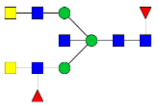
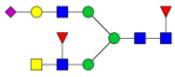
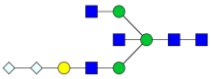
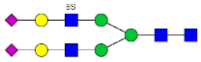
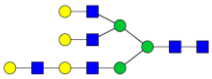
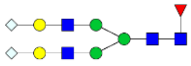
48	2241.7 $[M+Na]^+$	20.7		$Hex_3HexNAc_7dHex_2$
49	2288.7 $[M+Na]^+$	308.1		$Hex_4HexNAc_5NeuAc_1$ $dHex_2$
50	2317.6 $[M+Na]^+$	12.8		$Hex_4HexNAc_5NeuAc_2$
51	2325.1 $[M+Na]^+$	66.4		$Hex_5HexNAc_4NeuAc_2$
52	2393.6 $[M+Na]^+$	14.6		$Hex_7HexNAc_6$
53	2424.6 $[M+Na]^+$	12.3		$Hex_5HexNAc_4NeuAc_2$ $dHex_1$

Table S3. List of the significantly changed N-linked glycans between control and disease groups. (setting *p*-value less than 0.01 and fold change between two groups greater than 1.2)

m/z	p-value	fold change (Control/ Disease)
1282.3	0.00324	0.82
1298.3	0.00126	0.77
1339.3	0.00158	0.78
1444.4	0.00200	0.80
1460.3	0.00058	0.75
1485.4	0.00372	0.80
1501.4	0.00049	0.74
1647.4	0.00063	0.74
1663.4	0.00251	0.78
1688.5	0.00427	0.82
1704.4	0.00002	0.72
1809.5	0.00129	0.75
1816.5	0.00044	1.33
1825.5	0.00074	0.68
1850.5	0.00004	0.67
1866.5	0.00074	0.64
2012.6	0.00025	0.68
2028.6	0.00219	0.70