Supplementary Materials: Fabrication of Alkoxyamine-Functionalized Magnetic Core–Shell Microspheres via Reflux Precipitation Polymerization for Glycopeptide Enrichment

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The density of alkoxyamine group can be calculated according to TGA results. For the MSP@PNAMAm and MSP@PNAMAm, the final residual weight percentages of both two samples in 600 °C represented the inorganic magnetic core. For 1 g MSP@PNAMAm, we can use W_1/W_2 to represent the corresponding MSP@PNAMAm mass, and the differ $(W_1 - W_2)/W_2$ was caused by the deprotection, the loss of phthalimide group. So the mole of phthalimide in 1 g MSP@PNAMAm can be calculated by the formula below:

$$d = (W_1 - W_2)/(W_2 \times M_{pt}) \quad (1)$$

Where M_{pt} is the differ molecular weight caused by deprotection, the value is 132 g/mol. The d value could also represent the density of alkoxyamine group.

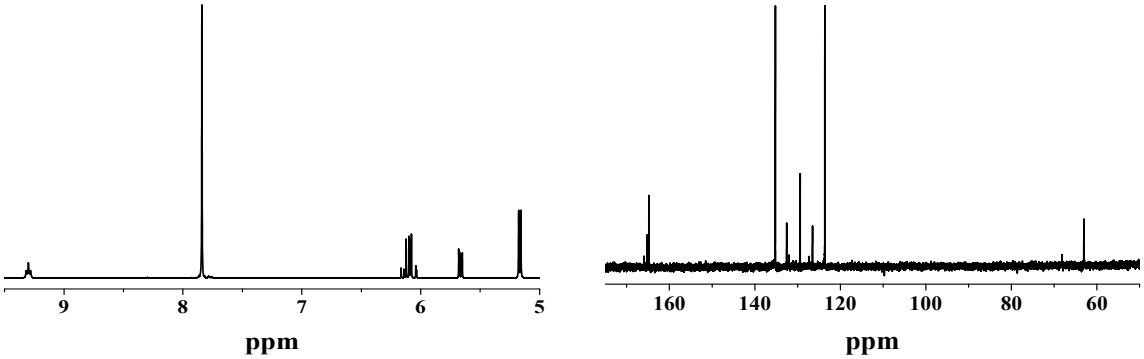

Figure S1. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR spectra of monomer NAMAm-*p*.

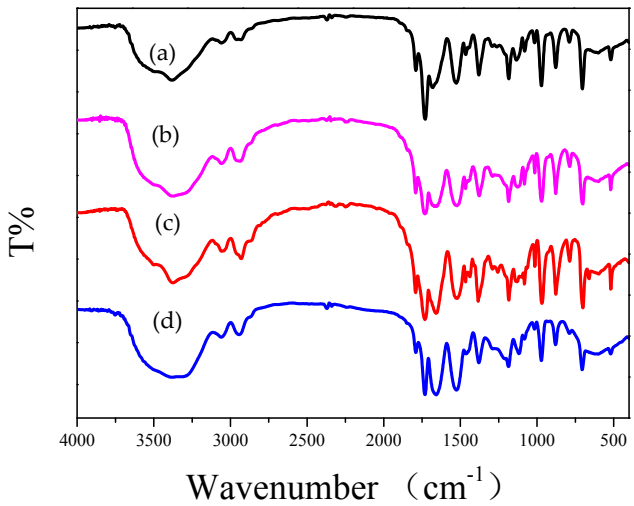

Figure S2.FT-IR spectra of PNAMAm-*p* microspheres prepared with different ratios of MBA; (**a**) 20%; (**b**) 30%; (**c**) 40%; (**d**) 50%.

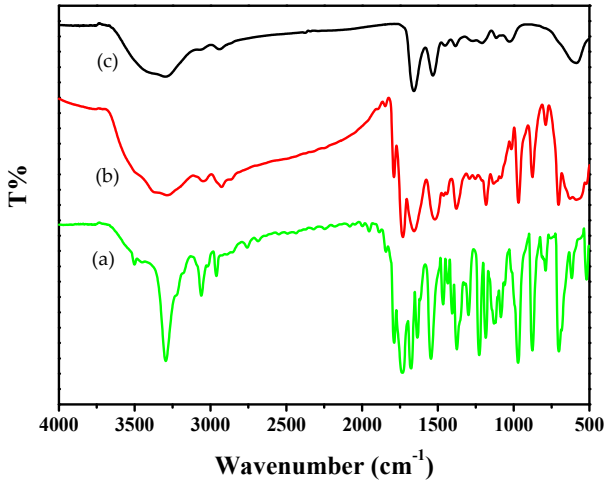

Figure S3. FT-IR spectra of (**a**) NAMAm-*p*, (**b**) MSP@PNAMAm-*p* and (**c**) MSP@PNAMAm.

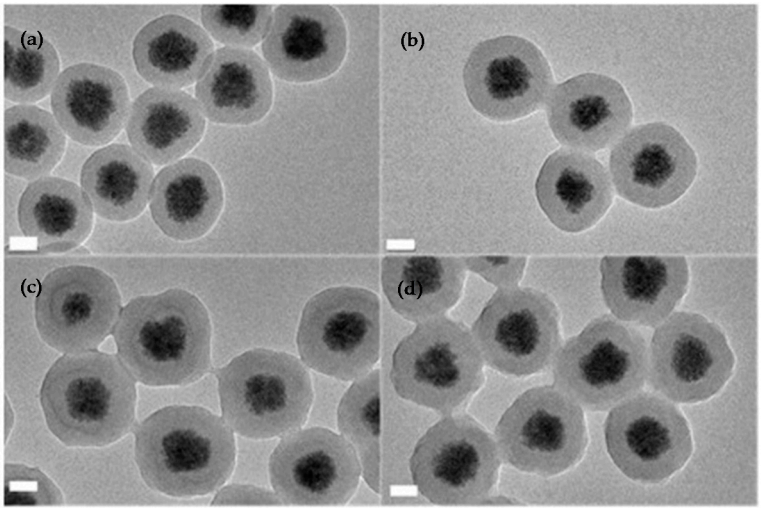

Figure S4.TEM images of MSP@PNAMAm-*p* with different ratios of NAMAm and MBA: (**a**) 4:1; (**b**) 7:3; (**c**) 3:2, (**d**) 1:1. The scale bar is 100 nm.

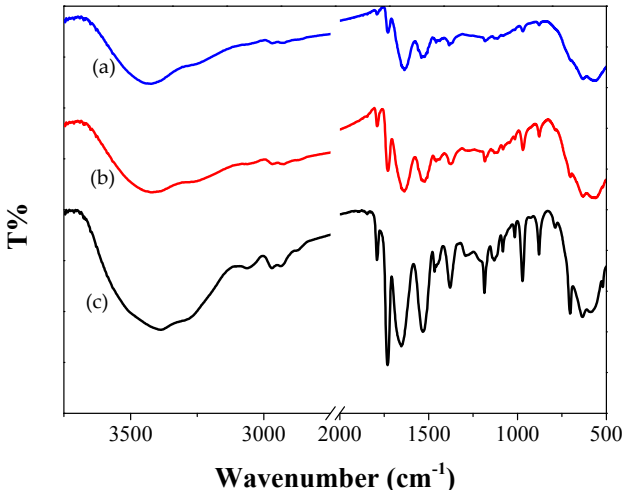

Figure S5. FT-IR Spectra of MSP@PNAMAm-*p*-*co*-PNIPAm with different ratios of NAMAm-*p* and NIPAm: (**a**) NAMAm-*p*:NIPAm = 1:3; (**b**) NAMAm-*p*:NIPAm = 1:1; (**c**) NAMAm-*p*:NIPAm = 3:1

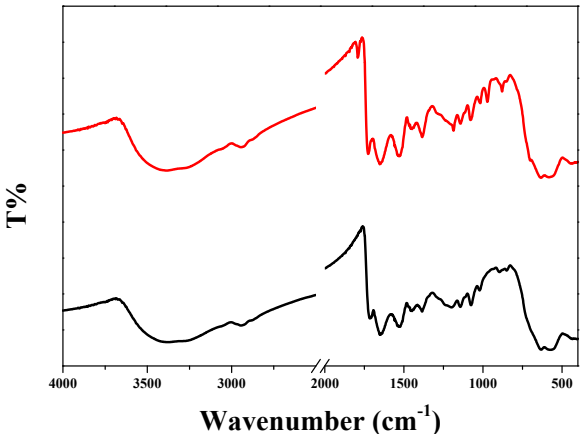

Figure S6. FT-IR Spectra of (**a**) MSP@PNAMAm-*p*-*co*-PAA and (**b**) MSP@PNAMAm-*co*-PAA.

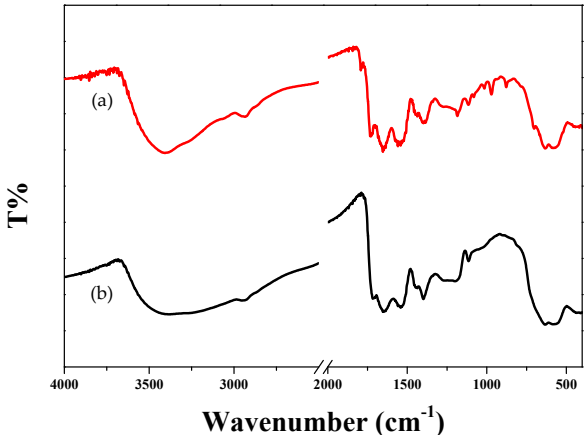

Figure S7. FT-IR Spectra of (**a**) MSP@PNAMAm-*p*-*co*-PHEMA and (**b**) MSP@PNAMAm-*co*-PHEMA.

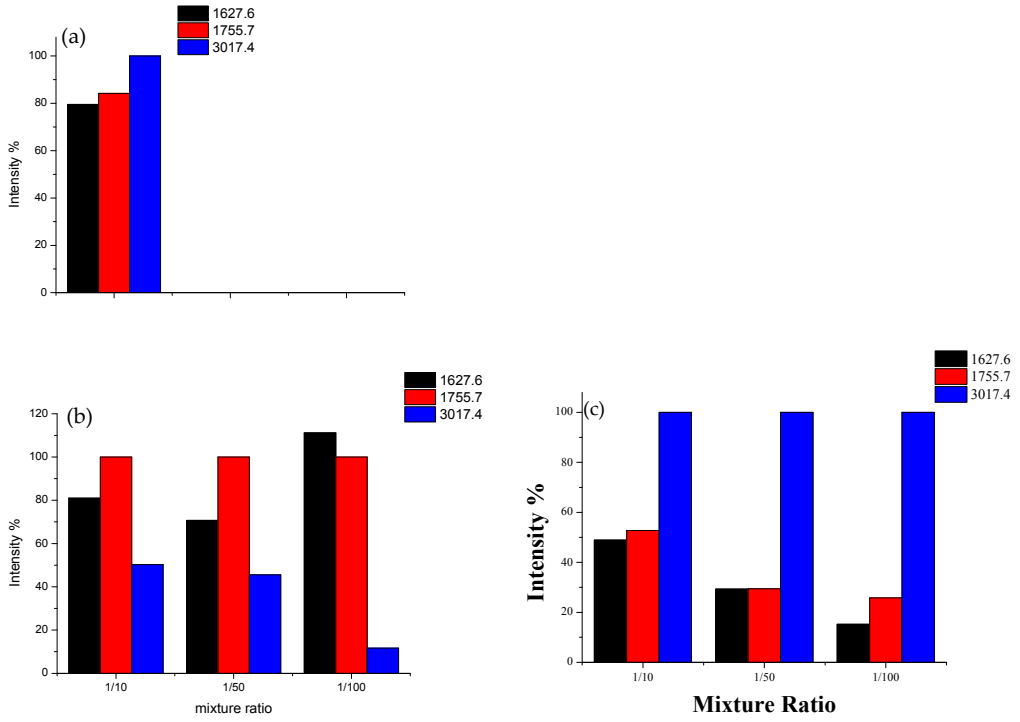

Figure S8. Relative intensity of different signal peaks. (**a**) tryptic digest of ASF following deglycosylation by PNGase F; (**b**) enriched by MSP@PNAMAm-1 in different mixture; (**c**) enriched by MSP@PNAMAm-4 in different mixture.

Table S1. List of identified glycoproteins from 5μL human serum after solid phase extraction with MSP@PNAMAm after three parallel runs, N# denotes the *N*-linked glycosylation site.

NO.	Protein	Description	Peptide
1.	Q9UQM7|KCC2A_HUMAN	Calcium/calmodulin-dependent protein	N#FSGGKSGGNK
2.	Q9ULV1|FZD4_HUMAN	Frizzled-4	ISMCQNLGYN#VTK
3.	Q9P2D1|CHD7_HUMAN	Chromodomain-helicase-DNA-binding protein	EN#ATNGVQQLSK EESMEIHATGKHSESNAELGQLYWPN#TSTLTTR
4.	Q9P225|DYH2_HUMAN	Dynein	QNN#VSVDSLSWEFIVSTVDDSNLVYPPK
5.	Q9NZR2|LRP1B_HUMAN	lipoprotein	SAEQSCN#SSFFMCKNGR
6.	Q9NUQ2|PLCE_HUMAN	acyltransferase	LYCVYQSMVLFFFEN#YTGVQILLYGDLPKNKENIIYLANHQSTVDWIVADILAIR
7.	Q96RI8|TAAR6_HUMAN	amine-associated receptor	MSSN#SSLLVAVQLCYANVN#GSCVKIPFSPGSR
8.	Q96PY0|K1908_HUMAN	Uncharacterized protein	GCGDSGSSGMAQRAQAGSN#QSRGK
9.	Q96MT8|CEP63_HUMAN	Centrosomal protein	AN#DTICANELEIER
10.	Q92752|TENR_HUMAN	Tenascin-R	GTN#ESDSATTQFTTEIDAPK
11.	Q8WXI2|CNKR2_HUMAN	Connector enhancer	TLSHKLN#ASAK
12.	Q8WVX9|FACR1_HUMAN	Fatty acyl-CoA	ASNNALADLVPVDVVVN#MSLAAAWYSGVNRPR
13.	Q8NHS9|SPT22_HUMAN	Spermatogenesis-associated protein	DGNKN#TSLK IPEPPN#LSRNK DGNKN#TSLKTWNK
14.	Q8NF91|SYNE1_HUMAN	Nesprin-1	VSQLSSQYLALSN#LTK
15.	Q8NE71|ABCF1_HUMAN	ATP-binding cassette	AANAAENDFSVSQAEMSSRQAMLEN#ASDIK
16.	Q8N9W8|FA71D_HUMAN	Protein FAM71D	KN#TSKTTMR FLPLQFVTLSVHDAEN#MSLK
17.	Q8N3K9|CMYA5_HUMAN	Cardiomyopathy-associated protein	SNYAQFISN#TSASNADKMVSNKEMPK IEAFVSEIESFFNTIEEN#CSKNEKR
18.	Q8JTG9|L_ABLVH	Large structural protein	LLN#YTLGNR VGGLAAQAMISLWLHGEHSESN#RSRK

Table S1. *Cont.*

NO.	Protein	Description	Peptide
19.	Q8IVL0|NAV3_HUMAN	Neuron navigator	SSPVTVN#QTDK EPTKIGSGRSSPVTVN#QTDK
20.	Q86U42|PABP2_HUMAN	Polyadenylate-binding protein	QMN#MSPPPGNAGPVIMSIEEK
21.	Q6TFL3|CC171_HUMAN	Coiled-coil domain-containing protein	MNLN#TSSNTGDTQR
22.	Q6SW37|EP84_HCMVM	Early phosphoprotein	N#NTRGGGGGGGGGRNSR
23	Q6P1J6|PLB1_HUMAN	Phospholipase B1	VLVNLVDFLN#PTIMR
24	Q2KJY2|KI26B_HUMAN	Kinesin-like protein	EDN#GSEGQLTNREGPELPASKMQR CSSGHGSDN#SSVLSGELPPAMGKTALFYHSGGSSGYESVMRDSEATGSASSAQDSTSEN#SSSVGGR
25.	Q16827|PTPRO_HUMAN	Receptor-type tyrosine-protein	QHRTAPYPPQN#ISVR
26.	Q16821|PPR3A_HUMAN	Protein phosphatase 1	EVLDDNANPAHGN#GTVQIPCPSSDQLMAGNLNK
27.	Q14558|KPRA_HUMAN	Phosphoribosyl pyrophosphate synthase-associated protein	N#ATVHPGLELPLMMAK
28	Q14527|HLTF_HUMAN	Helicase-like transcription	AGGVGLN#LSAASR EYNVNDDSMKLGGN#NTSEKADGLSK QICCHTYLLTNAVSSNGPSGN#DTPEELRKK
29	Q13901|C1D_HUMAN	Nuclear nucleic acid-binding protein	N#ASKVANKGK
30	Q13023|AKAP6_HUMAN	A-kinase anchor protein	N#GSDSLQRSTSLESWLTSYK TFTGMQNAKQLSLLSHSSSIESLSPGGDLFGLGIFKN#GSDSLQR
31.	Q12913|PTPRJ_HUMAN	Receptor-type tyrosine-protein	IHVAGETDSSNLN#VSEPR TNAIQVFDVTAVN#ISATSLTLIWKVSDN#ESSSNYTYK
32.	Q12879|NMDE1_HUMAN	Glutamate receptor	INN#STNEGMNVK FVKIN#NSTNEGMNVK KKSPDFN#LTGSQSNMLK
33.	Q06187|BTK_HUMAN	Tyrosine-protein	N#GSLKPGSSHRK EGSMSEDEFIEEAKVMMN#LSHEK

Table S1. *Cont.*

NO.	Protein	Description	Peptide
34.	P56524|HDAC4_HUMAN	Histone deacetylase 4	ILIVDWDVHHGN#GTQQAFYSDPSVLYMSLHR
35.	P49792|RBP2_HUMAN	E3 SUMO-protein	N#GSLRNADSEIKHSTPSPTR N#VSGISFTENMGSSQQKNSGFRR EMLNSVMQELEDYSEGGPLYKN#GSLRNADSEIK
36.	P32004|L1CAM_HUMAN	Neural cell adhesion	HQMAVKTN#GTGR YFCLAANDQNN#VTIMANLKVK
37.	P20936|RASA1_HUMAN	Ras GTPase-activating protein	EPVPMQDQEQVLN#DTVDGKEIYNTIRR
38	P20592|MX2_HUMAN	Interferon-induced GTP-binding protein	SVMNVVRN#LTYPLK
39	P20273|CD22_HUMAN	B-cell receptor	RTQSQQGLQEN#SSGQSFFVRNK
40.	P19827|ITIH1_HUMAN	Inter-α-trypsin	DKICDLLVANNHFAHFFAPQN#LTNMNK
41.	P09871|C1S_HUMAN	Complement C1s	VKNYVDWIMKTMQEN#STPR
42.	P05877|ENV_HV1MN	Envelope glycoprotein	N#TTNTNNSTANN#NSNSEGTIK N#TTNTN#NSTANN#NSNSEGTIKGGEMK
43	P05155|IC1_HUMAN	C1 inhibitor	VGQLQLSHN#LSLVILVPQNLK
44	P04196|HRG_HUMAN	Histidine-rich glycoprotein	VEN#TTVYYLVLDVQESDCSVLSR
45.	P04114|APOB_HUMAN	Apolipoprotein	SYN#ETKIKFDK LNGESNLRFN#SSYLQGTNQITGR
46	P02790|HEMO_HUMAN	Hemopexin	SWPAVGN#CSSALR
47	P02787|TRFE_HUMAN	Serotransferrin	QQQHLFGSNVTDCSGNFCLFR ILRQQQHLFGSNVTDCSGNFCLFR
48	P02749|APOH_HUMAN	β-2-glycoprotein	VYKPSAGN#NSLYR MEILDNN#WTALLELWDERHR ELAVN#KTQLENIQKTGQEMIEGGHYASDN#VTTR
49	P01876|IGHA1_HUMAN	Ig α-1	LAGKPTHVN#VSVVMAEVDGTCY LSLHRPALEDLLLGSEAN#LTCTLTGLR

Table S1. *Cont.*

NO.	Protein	Description	Peptide
50	P01871|C1S_HUMAN	Ig mu	YKN#NSDISSTR
51	P01857|IGHG1_HUMAN	Ig γ	EEQYN#STYR EEQYN#STYRVVSVLTVLHQDWLNGK
52	P01024|CO3_HUMAN	Complement C3	TVLTPATNHMGN#VTFTIPANR
53	P01023|A2MG_HUMAN	α-2-macroglobulin	VSNQTLSLFFTVLQDVPVR
54	P01011|AACT_HUMAN	α-1-antichymotrypsin	TLNQSSDELQLSMGNAMFVKEQLSLLDR
55	P01009|A1AT_HUMAN	α-1-antitrypsin	YLGNATAIFFLPDEGK
56	P00738|HPT_HUMAN	Haptoglobin	NLFLN#HSEN#ATAK VVLHPN#YSQVDIGLIK MVSHHN#LTTGATLINEQWLLTTAK GSFPWQAKMVSHHN#LTTGATLINEQWLLTTAK
57	O95714|HERC2_HUMAN	ubiquitin-protein	SLN#VSSSVNQASR DAPHSEGDMHLLSGPLSPN#ESFLR
58.	O15297|PPM1D_HUMAN	Protein phosphatase	IHDSLNNSLPIGLVPTN#STNTVMDQK
59	O00141|SGK1_HUMAN	Serine/threonine-protein	RMGLNDFIQKIAN#NSYACK
60	F5HB53|GB_HCMVM	Envelope glycoprotein B	SSLN#LTHNRTK
61	B1NKQ9|RDRP_ROTH7	RNA-directed RNA polymerase	IIRVDGDDNYAVLQFNTEVTKQMVQN#VSNDVR
62	A8MTB9|CEA18_HUMAN	cell adhesion molecule	MN#LSSLAWEQMGRYR VNREGSLLIRPTALN#DTGN#YTVR
63.	A4UHQ7|L_EBLV2	RNA-directed RNA polymerase	LLN#YTLENRGLAIPTDGVLSSLK
64	A1L390|PKHG3_HUMAN	Pleckstrin	NGAGSLRSRHLPNSNN#NSSSWLNVK HLPNSNN#NSSSWLNVKGPLSPFNSR