

Electronic Supplementary Information

for

**Ti⁴⁺-immobilized Phosphate Polymer-patterned Silicon Substrate for
On-plate Selective Enrichment and Self-desalting of Phosphopeptides**

Lei Xu,^a Wei Zhu,^c Rui Sun,^a and Yin Ding*^{a, b}

a. State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, 22 Hankou Road, Nanjing 210093, China

b. Huai'an High-Tech Research Institute of Nanjing University, Huai'an 223005, PR China

c. Department of Oncology, First Affiliated Hospital of Nanjing Medical University, 300 Guangzhou Road, Nanjing 210029, PR China

* To whom correspondence should be addressed: Dr. Yin Ding, phone/fax 86-25-8368 6106, E-mail dingyin@nju.edu.cn

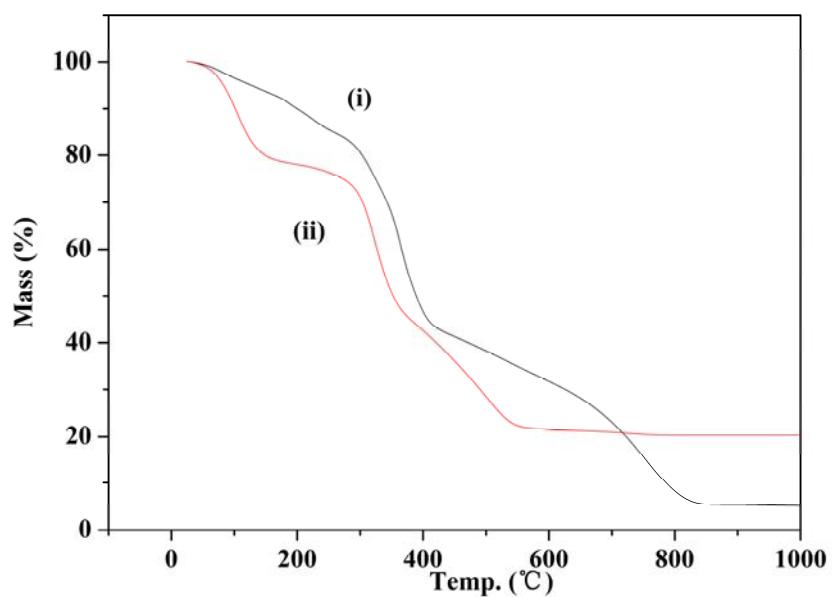


Fig. S1. TGA curves of: (i) poly(MAA-HEMAP); (ii) poly(MAA-HEMAP)-Ti⁴⁺.

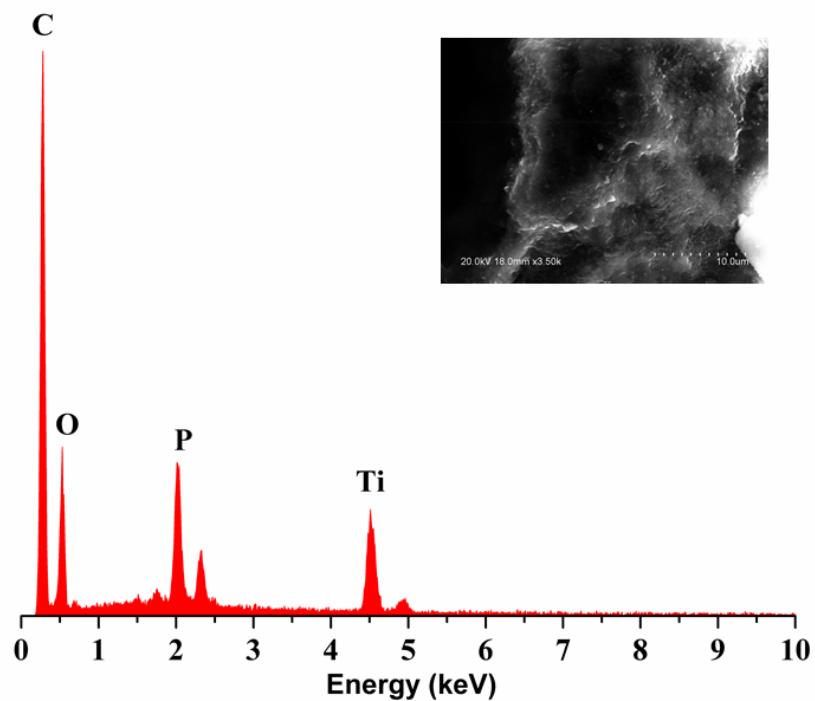
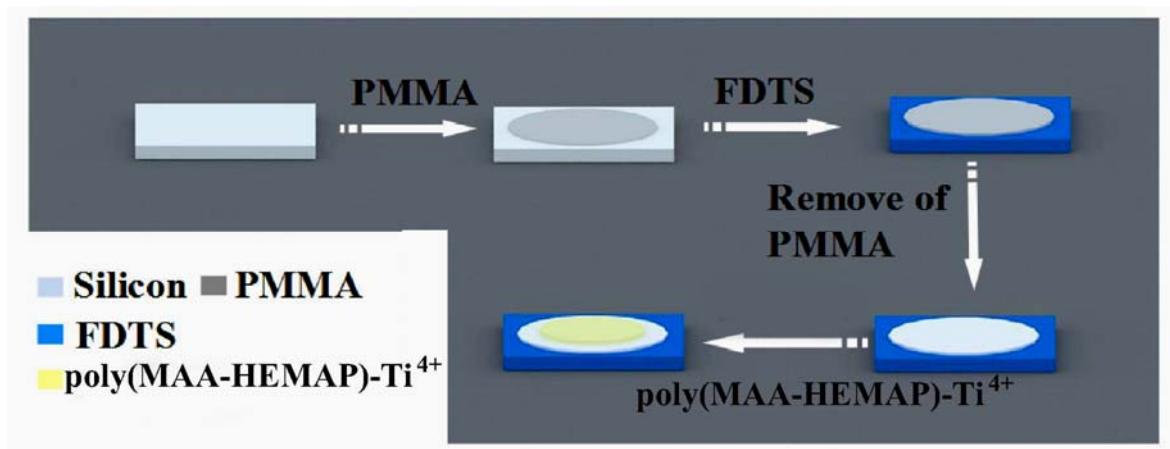


Fig. S2. The energy dispersive X-ray (EDX) spectrum data of poly(MAA-HEMAP)-Ti⁴⁺

Table S1. The energy dispersive X-ray (EDX) spectrum data of poly(MAA-HEMAP)-Ti⁴⁺

Element	Wt%	At%
C K	65.69	76.10
O K	22.76	19.79
P K	4.75	2.14
Ti K	6.79	1.97



Scheme S1. Schematic illustration for the preparation of the patterned sample support.

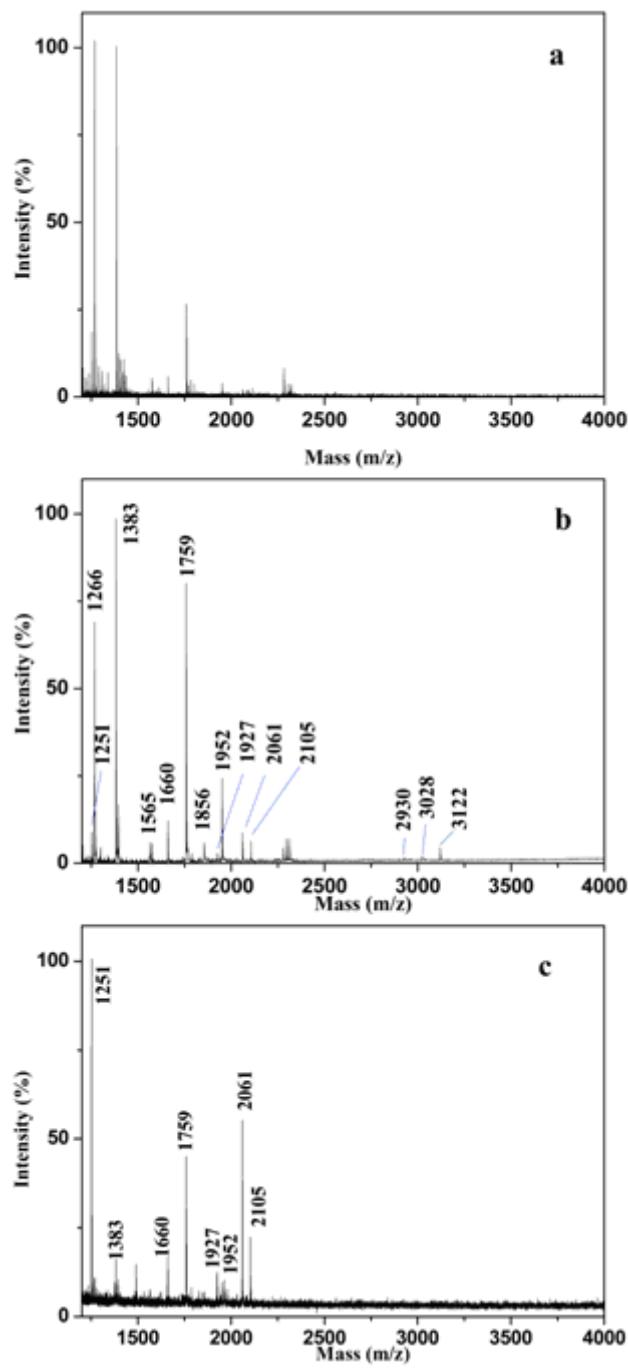


Fig. S3. Mass spectra of the peptides: casein (1.5×10^3 fmol μL^{-1}) obtained with (a) the traditional MALDI plate and the patterned sample support: the concentration of casein are (b) 15 fmol μL^{-1} ; (c) 5 fmol μL^{-1} , respectively.

Table S2. Peptides detected in the sample by using the patterned sample support

peak number	observed m/z	aa	amino acid sequence	References
1	1251	α -S2(213–222)	TKVIPYVRYL	1
2	1266	α -S1(91–100)	YLGYLEQLLR	1, 2, 5
3	1337	α -S1/52–73	VNELpSKDIGpSEpSTEDQAMEDIK	1, 2, 4, 5
4	1383	α -S1(38–49)	FFVAPFPEVFGK	1, 2, 5
5	1466	α -S2(153–164)	TVDMESTEVFTK	2, 4
6	1565	beta-casein(1-25)	RELEELNVPGEIYESLSSSEESITR	3, 5
7	1637	α -S1(106–118)	YLGYLEQQLRLKK	1, 6
8	1641	α -S1(38–51)	FFVAPFPEVFGKEK	1
9	1660	α -S1(121–134)	VPQLEIVPNSAEER	2, 4, 5, 6
10	1759	α -S1(23–37)	HQGLPQEVLNENLLR	1, 2, 5
11	1832	α -S1(106–120)	YLGEYLIVPNSAEER	4, 6
12	1848	α -S1(58–73)	DIGpSETEDQAMEDIK	1, 2
13	1856	α -S1(119–134)	DIGpSEpSTEDQAMEDIK	5
14	1927	α -S1(43–58)	DIGpSEpSTEDQAMEDIK	2, 4, 1
15	1952	α -S1(119–134)	YKVPQLEIVPNSAEER	2, 3, 4, 5, 6
16	2029		KEESEESDDDMGFGLFD	2
17	2061	beta-casein (33–48)	FQ-pS-EQQQTEDELQDK	3, 6
18	2105	α -S1(189–208)	TDAPSFSIDPNPIGSENSEK	1
19	2559	beta-casein(33–52)	FQSEEQQQTEDELQDKIHPF	3, 6
20	2736	α -S1(74–94)	Q-oxM-EAESISSSEEIVPNSVEQK	6
21	2930	α -S1(49–74)	KEKVNELpSKDIGpSEpSTEDQAMEDIKQ	2, 4
22	3028	beta-casein(1-25)	RELEELNVPGEIYESLSSSEESITR	2, 3, 6
23	3122	beta-casein(/1-25)	RELEELNVPGEIYESLSSSEESITR	2, 3, 6

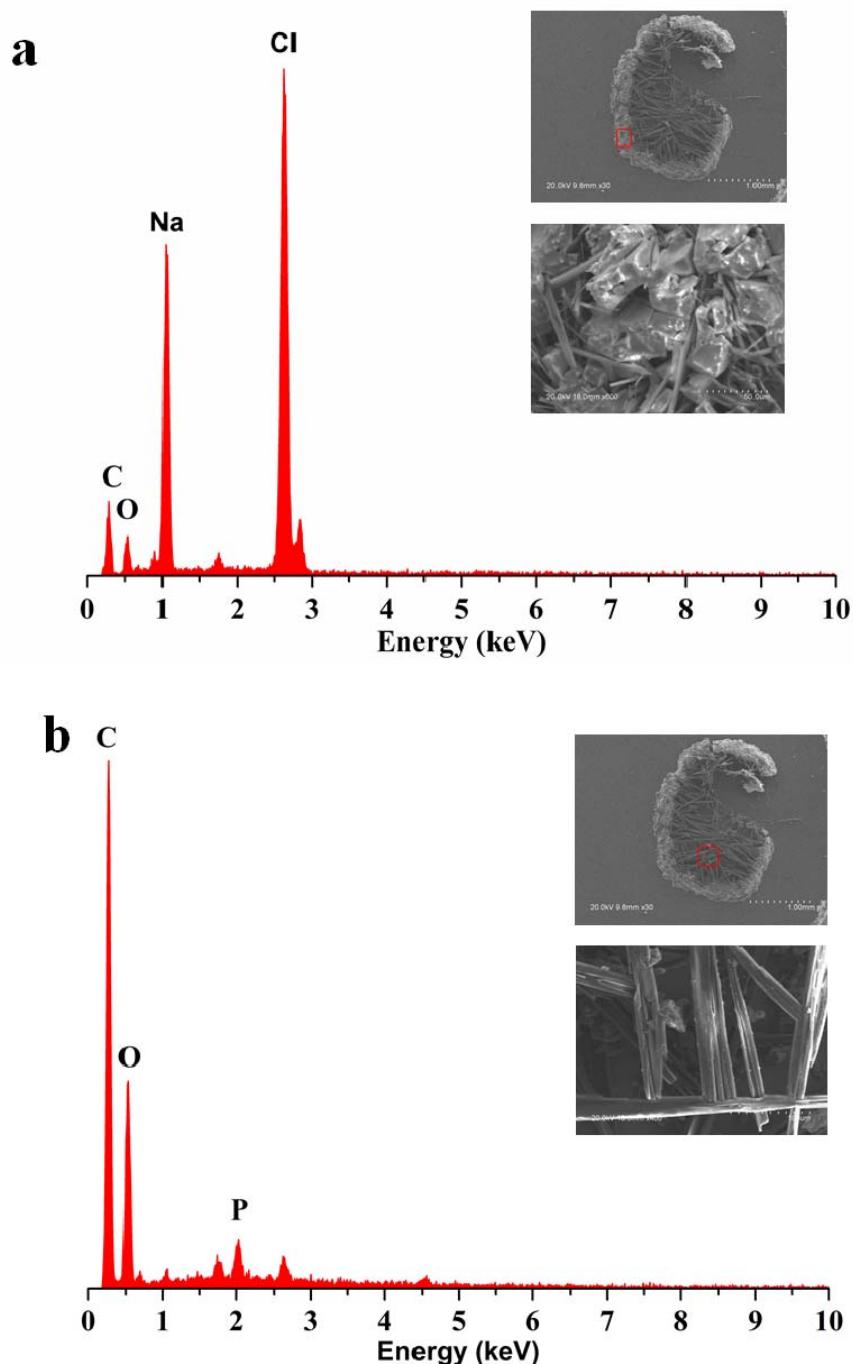


Fig. S4. EDX/SEM images of salt-containing sample preparation on the patterned sample support: (a) the salt contaminants are separated from the analytes. (b) the analyte-matrix co-crystallizations are distributed in the centre polymer surface.

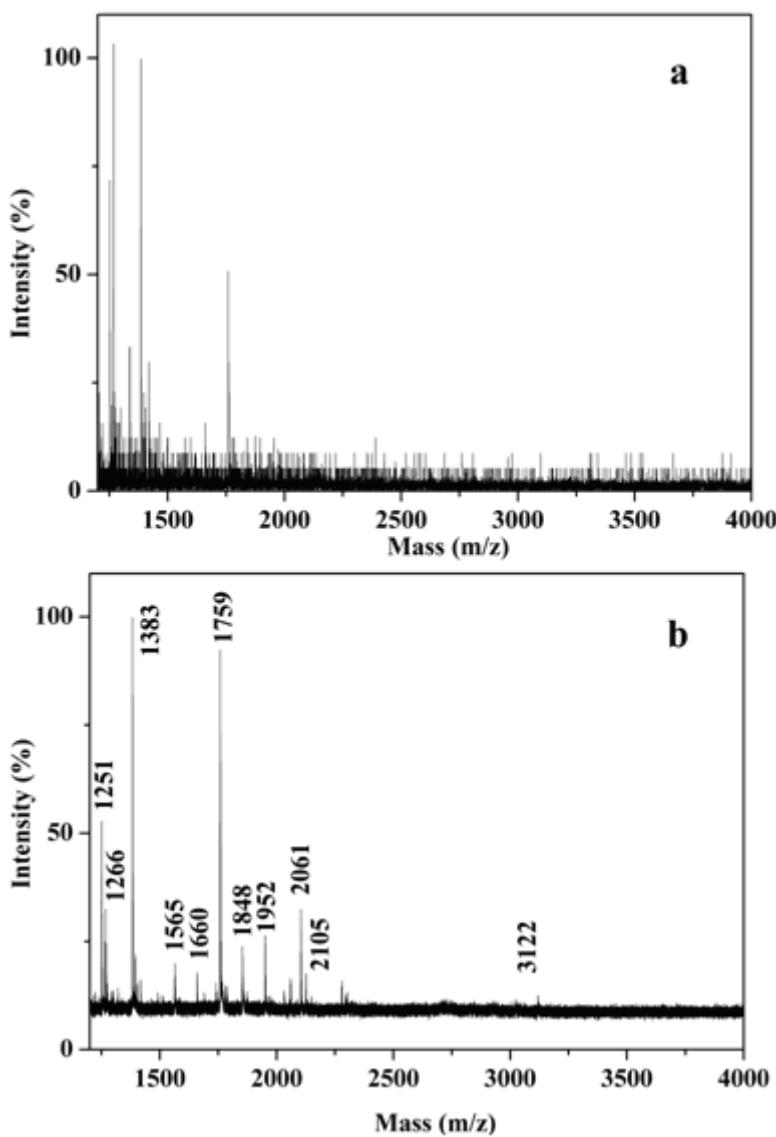


Fig. S5. Mass spectra of the peptides: human serum obtained with (a) the traditional MALDI plate and (b) the patterned sample support, respectively.

References

- 1 S. K. Kailasa and H. F. Wu, *Microchim. Acta*, 2012, **179**, 83.
- 2 H. Y. Zhong, X. Xiao, S. Zheng, W. Y. Zhang, M. J. Ding, H.Y. Jiang, L. L. Huang and J. Kang, *Nat. Commun.*, 2013, **4**, 1656.
- 3 Z.G. Wang, G. Cheng, Y. L. Liu, J. L. Zhang, D. H. Sun and J. Z. Ni, *Small*, 2012, **8**, 3456.
- 4 H. Li, X. Z. Shi, L. Z. Qiao, X. Lu and G. W. Xu, *J. Chromatogr. A*, 2013, **1275**, 9.
- 5 R. Grady, M. V. Blacken, V. Tomáš, S. Martin and T. František, *Anal. Chem.*, 2007, **79**, 5449.
- 6 L. Krásný, P. Pompach, M. Strohalm, V. Obsilova, M. Strnadová, P. Nováka and M. Volnýa, *J. Mass Spectrom.*, 2012, **47**, 1294.