

## Supporting information

### Phytic acid functionalized bimetallic-based magnetic metal-organic frameworks for phosphopeptide enrichment

Shuang Yan, Bin Luo, Jia He, Fang Lan\* and Yao Wu\*

National Engineering Research Center for Biomaterials, Sichuan University, Chengdu  
610064, China

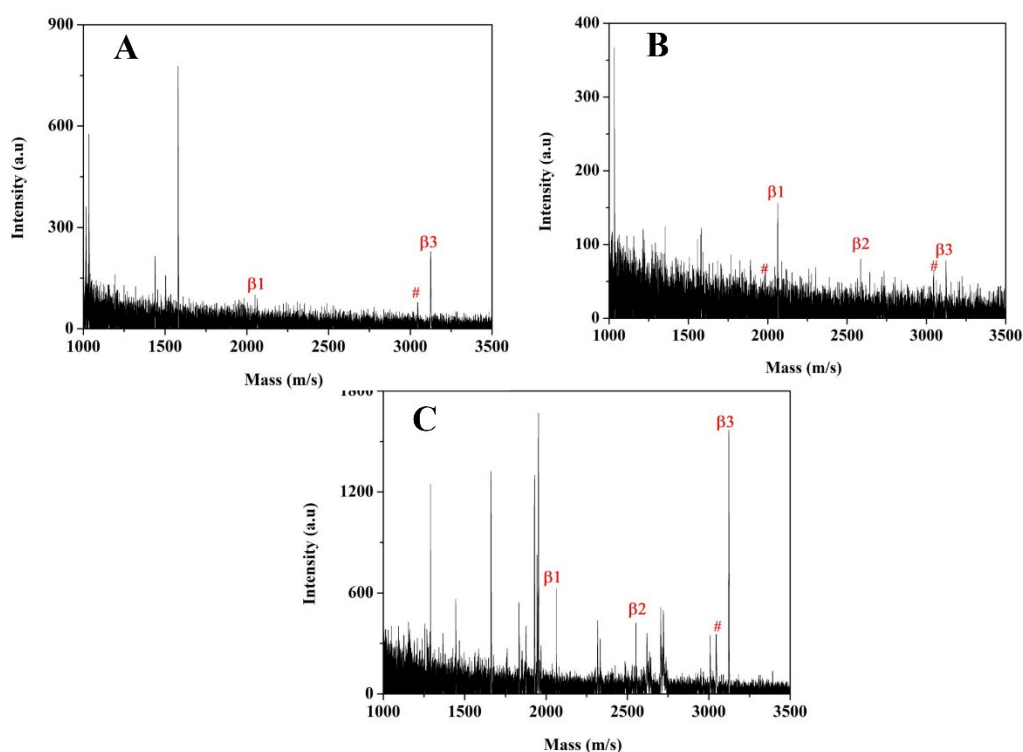


Figure S1. MALDI-TOF mass spectra of tryptic digests from  $\beta$ -casein ( $10^{-9}$  M) after enrichment by loading buffer (ACN/H<sub>2</sub>O/TFA=50/48/2) and elution (0.4 M NH<sub>3</sub>·H<sub>2</sub>O) (A) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Ce<sub>0.05</sub>-Zr-MOF@PA, (B) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Ce<sub>0.45</sub>-Zr-MOF@PA, (C) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Ce<sub>0.3</sub>-Zr-MOF@PA respectively. (#, dephosphorylated peptide)

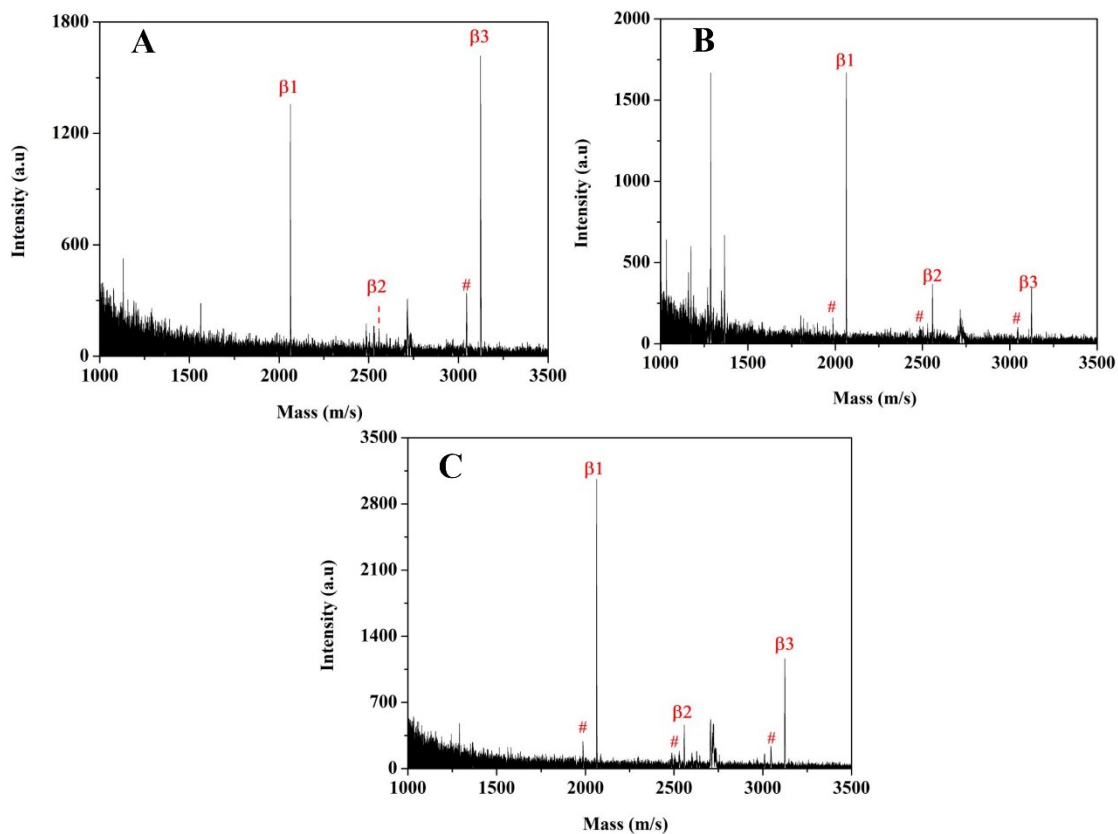


Figure S2. MALDI-TOF mass spectra of tryptic digests from  $\beta$ -casein ( $10^{-9}$  M) after enrichment by loading buffer (ACN/H<sub>2</sub>O/TFA=50/48.5/1.5) and elution (0.4 M NH<sub>3</sub>·H<sub>2</sub>O) (A) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Ce<sub>0.05</sub>-Zr-MOF@PA, (B) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Ce<sub>0.45</sub>-Zr-MOF@PA, (C) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Ce<sub>0.3</sub>-Zr-MOF@PA respectively. (#, dephosphorylated peptide)

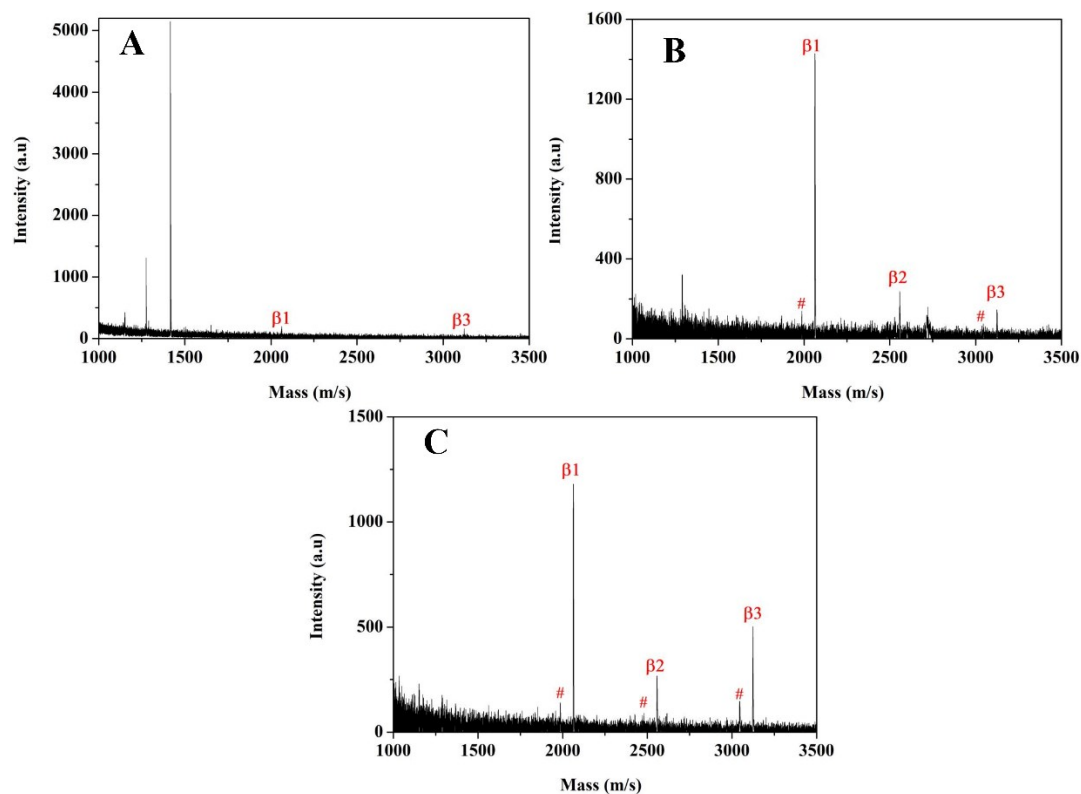


Figure S3. MALDI-TOF mass spectra of tryptic digests from  $\beta$ -casein ( $10^{-9}$  M) after enrichment by loading buffer (ACN/H<sub>2</sub>O/TFA=50/49/1) and elution (0.4 M NH<sub>3</sub>·H<sub>2</sub>O) (A) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Ce<sub>0.05</sub>-Zr-MOF@PA, (B) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Ce<sub>0.45</sub>-Zr-MOF@PA, (C) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Ce<sub>0.3</sub>-Zr-MOF@PA respectively. (#, dephosphorylated peptide)

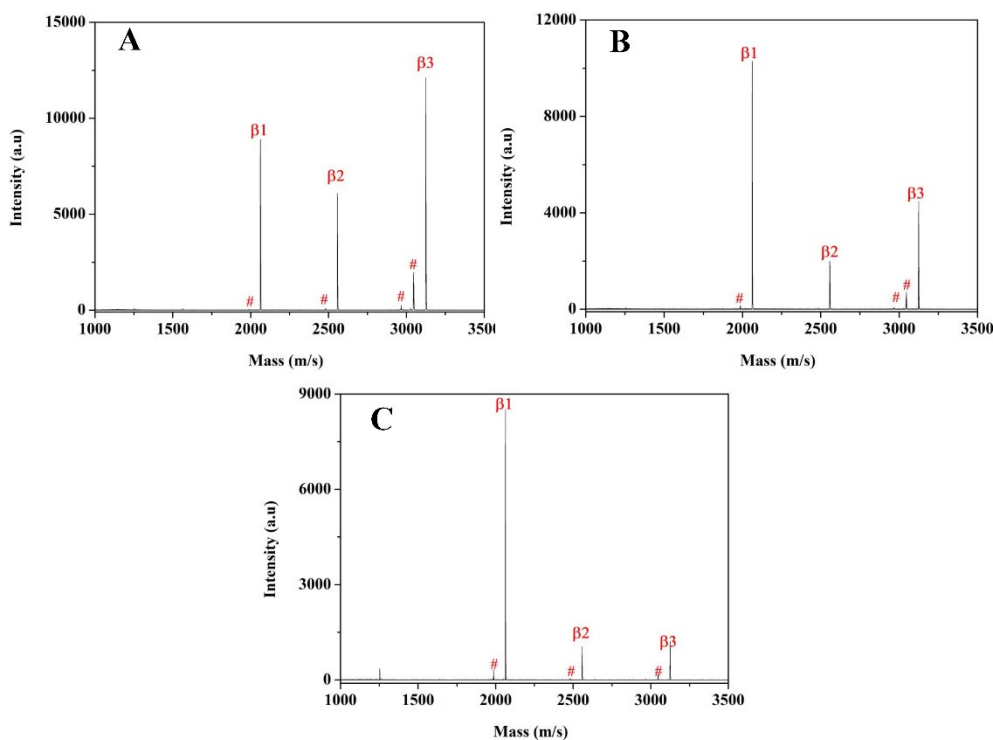


Figure S4. MALDI mass spectra of  $\beta$ -casein digest ( $10^{-6}$  M) after enrichment by  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Ce-Zr-MOF}@PA$  in 50%ACN-1%TFA, 0.4 M  $\text{NH}_3\cdot\text{H}_2\text{O}$ . (A) Cycling 1st, (B) cycling 3rd, and (C) cycling 5th (#, dephosphorylated peptide).

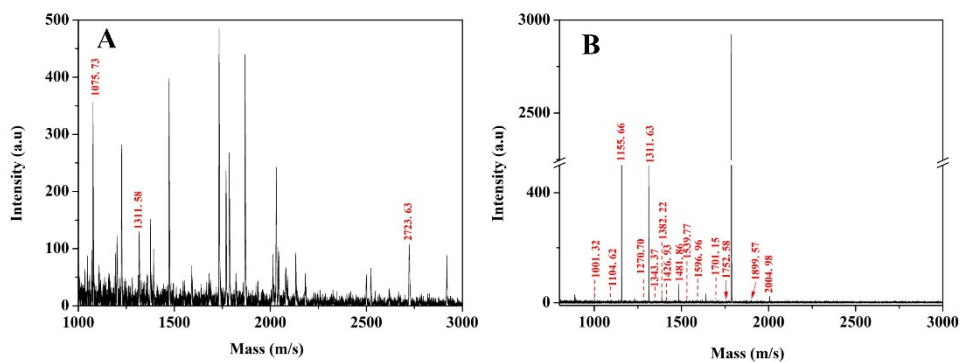


Figure S5. MALDI mass spectra of human saliva before (A) and after (B) enrichment by  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Ce-Zr-MOF}@PA$ . The peaks of phosphopeptides were marked with asterisks.

Table S1. Detail information of the observed phosphopeptides obtained from tryptic digest of  $\alpha$ -casein after enrichment by  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Ce-Zr-MOF}@PA$  in MALDI-TOF MS analysis

No.	Observed m/z	Peptides sequence	Number of phosphorylation
-----	--------------	-------------------	---------------------------

1	1237.66	TVDME[pS]TEVF	1
2	1411.45	EQL[pS]T[pS]EENSK	2
3	1467.32	TVDME[pS]TEVFIK	1
4	1662.30	VPQLEIVPN[pS]AEER	1
5	1833.44	YLGEYLIVPN[pS]AEER	1
6	1847.68	DIGSE[pS]TEDQAMEDIK	1
7	1927.28	DIG[pS]E[pS]TEDQAMEDIK	2
8	1943.28	DIG[pS]E[pS]TEDQA[Mo]EDI K	2
9	1952.54	YKVPQLEIVPN[pS]AEER	1
10	2490.02	AMKPWIQPKTKVIP[pY]VR[p Y]L	2
11	2576.03	Q[Mo]EAE[pS]I[pS][pS]SEEIV PNSVEQK	3
12	2607.45	EDVPSE[pY]LG[pY]LEQLL RLKK	2
13	2618.10	NTMEHV[pS][pS][pS]EESII[p S]QETKYK	4
14	2677.46	VNEL[pS]KDIG[pS]E[pS]TED QAMEDIK	3
15	2703.04	QMEAE[pS]I[pS][pS][pS]EEIV PN[pS]VEQK	5
16	2720.04	Q[Mo]EAE[pS]I[pS][pS][pS]EE IVPN[pS]VEQK	5
17	2746.14	HIQKEDVP[pS]ER[pY]LGYL EQLLR	2
18	2927.68	RELEELNVPGEIVESL[pS][pS ][pS] EESITR	3
19	2934.14	KEKVNEL[pS]KDIG[pS]E[pS] TEDQAMEDIKQ	3
20	2965.26	RELEELNVPGEIVE[pS]L[pS][ pS][pS]EESITR	4
21	3007.09	NANEEYSIG[pS][pS][pS]EE[ pS]AEVATEEVK	4
22	3041.79	RELEELNVPGEIVE[pS]L[pS][ pS]SEESITR	3
23	3087.95	NANEEY[pS]IG[pS][pS][pS] EE[pS]AEVATEEVK	5
24	3122.31	RELEELNVPGEIVE[pS]L[pS][ pS][pS]EESITR	4

Table S2. Detailed information of the detected phosphorylated peptides from non-fat milk digest after enriched by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Ce-Zr-MOF@PA in MALDI-TOF MS analysis.

<b>m/z(Da)</b>	<b>Number of phosphate groups</b>	<b>Peptide sequence</b>
3121.12	4	RELEELNVPGEIVE[pS]L[pS][pS][pS]EESITR
3022.97	3	RELEELNVPGEIVESL[pS] [pS][pS]EESITR
3007.82	4	NANEEEEYSIG[pS] [pS] [pS]EE[pS]AEVATEESITR
2963.98	4	ELEELNVPGEIVE[pS]L[pS][pS][pS]EESITR
2950.13	3	KEKVNEL[pS]KDIG[pS]E[pS]TEDQA[Mo]EDIKQ
2934.10	3	EKVNEL[pS]KDIG[pS]E[pS]TEDQAMEDI
2866.03	2	KVNELSKDIG[pS]E[pS]TEDQAMEDIKQ
2808.25	3	KVNEL[pS]KDIG[pS]E[pS]TEDQAMEDIK
2720.90	5	QMEAE [pS]L[pS] [pS] [pS]EEIVPN [pS] VEQK
2704.91	5	QMEAE [pS]L[pS] [pS] [pS]EEIVPN [pS] VEQK
2551.76	1	FQ[pS]EEQQQTEDELQDKIHPF
2352.20	4	NVPGEIVESL[pS][pS][pS]EE[pS]ITR
1926.18	2	DIG[pS]E[pS]TEDQAMEDIK
1632.47	1	ED [pS]PEVIESPPEIN
1561.39	4	RELEELNVPGEIVE[pS]L[pS][pS][pS]EESITR
1521.83	4	VVRNANEEEEYSI [pS] [pS] [pS]EE [pS] AEVATEEVKITVDDKHYQKAL
1494.51	2	RFFVAPFPEVFGKEKVNELSKDIG[pS]E[pS]TEDQA MEDIKQME
1281.07	1	KKIEKFQ[pS]EEQQQTEDELQDKIHPFAQ
1163.73	1	RINKKIEKFQ [pS]EEQQQTEDELQDKIHPFAQTQS

pS: phosphorylated site.