Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B

Supporting Information

Magnetic γ-Fe_2O_3@$REVO_4$ (RE=Sm, Dy, Ho) Affinity Microspheres for Selective Capture, Fast Separation and Easy Identification of Phosphopeptides

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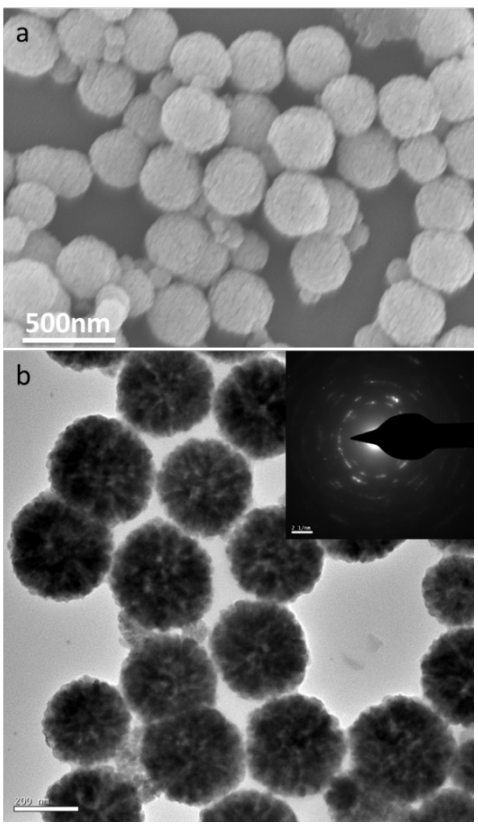

Fig. S1 SEM (a) and TEM (b) images of the Fe_3O_4 particles. Inset is the Selected Area Electron Diffraction (SAED) pattern.

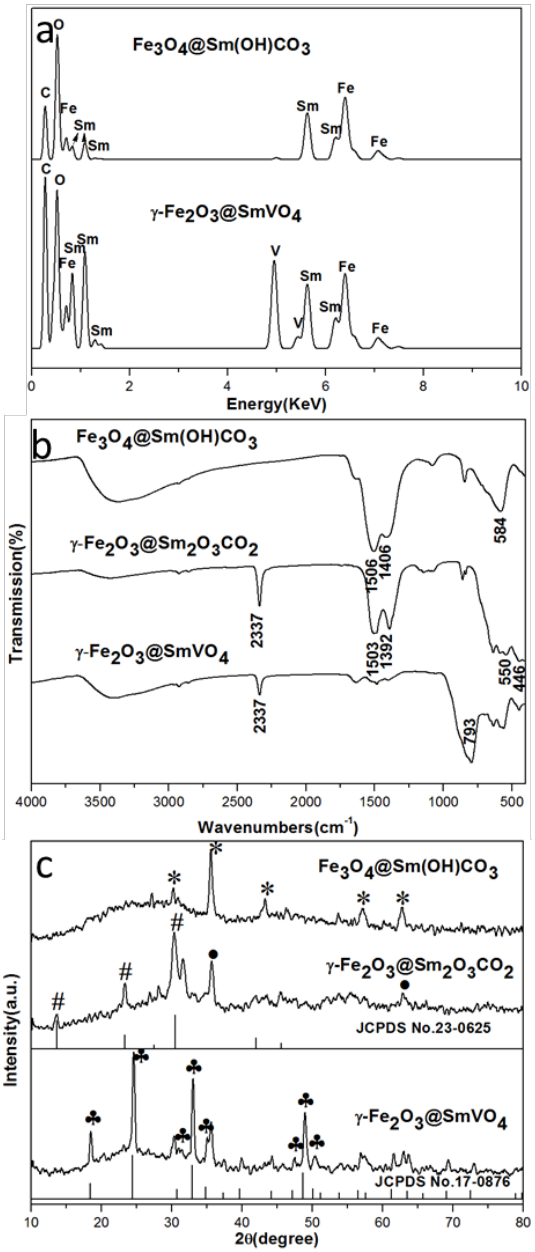

Fig. S2 EDS spectra (a), XRD patterns (b), and FTIR spectra (c) of the Fe_3O_4@Sm(OH)CO_3, γ-Fe_2O_3@$Sm_2O_3CO_2$ and γ-Fe_2O_3@$SmVO_4$ samples.

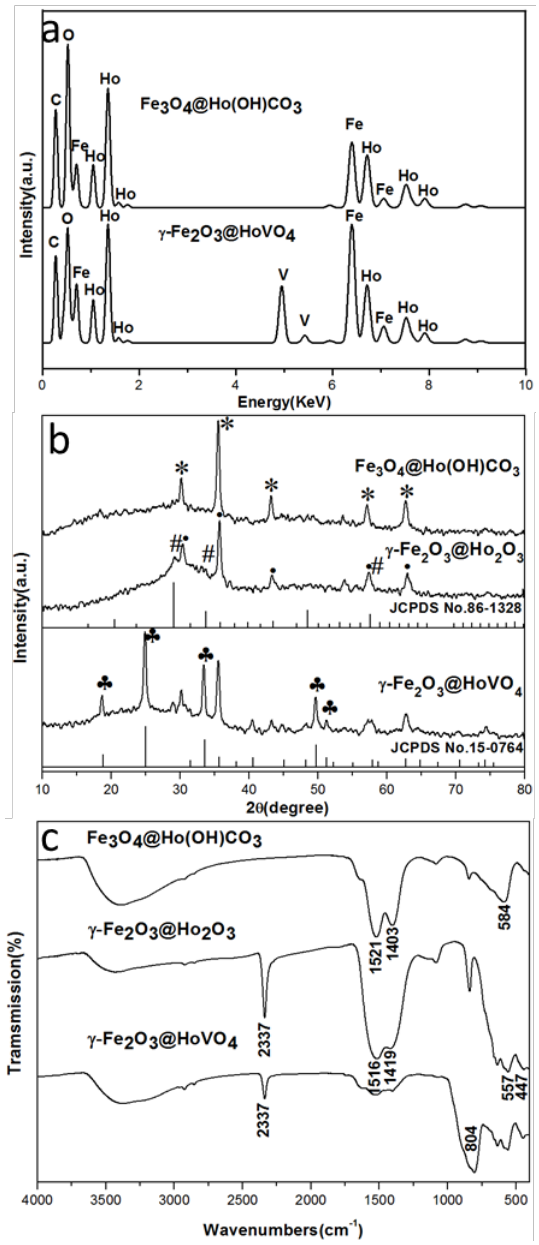

Fig. S3 EDS spectra (a), XRD patterns (b), and FTIR spectra (c) of the Fe_3O_4@Dy(OH)CO_3, γ-Fe_2O_3@Ho_2O_3 and γ-Fe_2O_3@$HoVO_4$ samples.

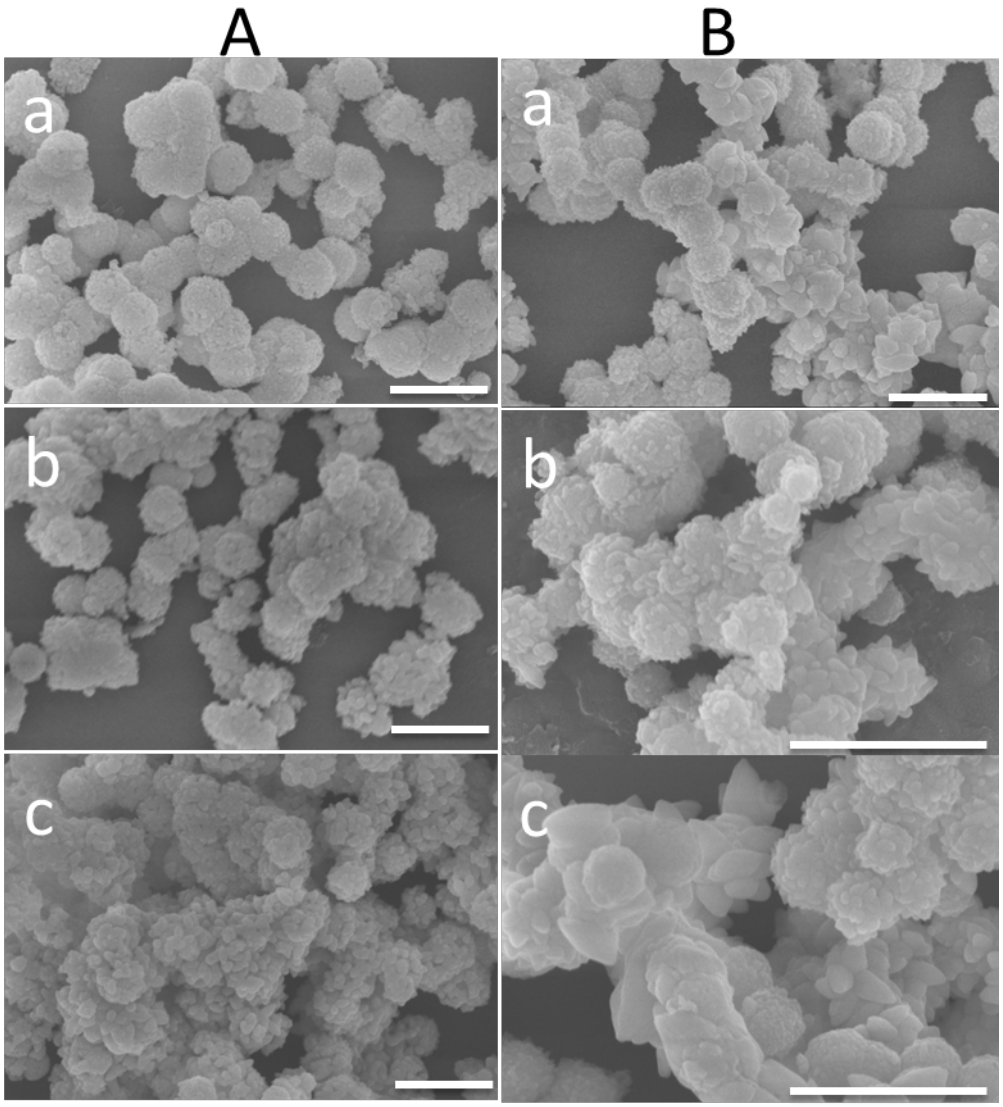

Fig. S4 SEM images :
Column A: a) Fe_3O_4@$SmVO_4$, b) Fe_3O_4@$DyVO_4$, and c) Fe_3O_4@$HoVO_4$ microspheres synthesized using Fe_3O_4@$RE(OH)CO_3$ as precursors with stirring.
Column B: a) γ-Fe_2O_3@$SmVO_4$, b) γ-Fe_2O_3@$DyVO_4$, and c) γ-Fe_2O_3@$HoVO_4$ synthesized using the γ-Fe_2O_3@RE_2O_3 microspheres as precursors without stirring.
Scale bars: 1 μm

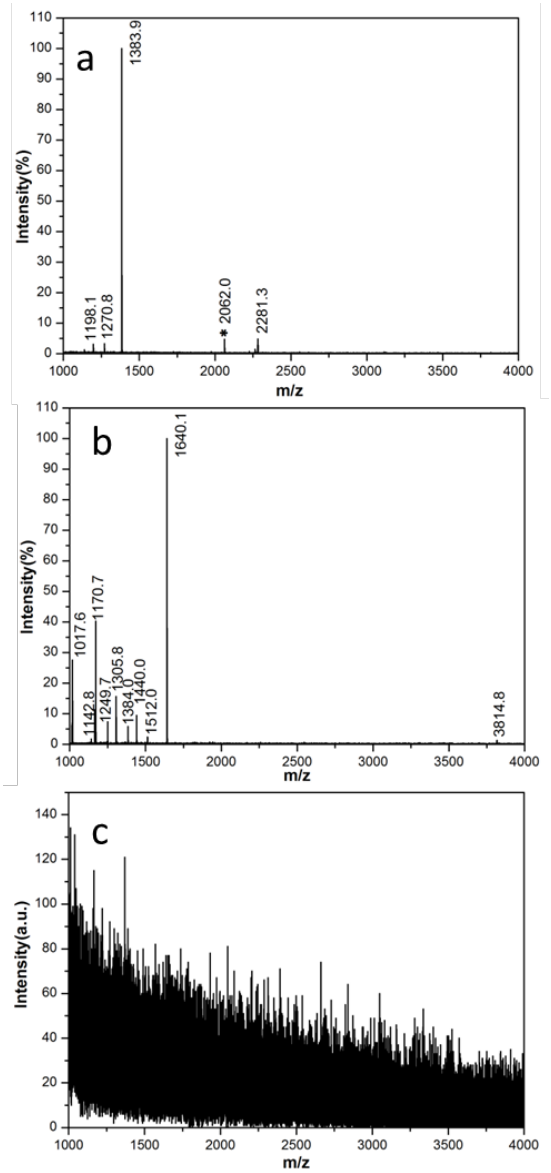

Fig. S5 MALDI-TOF mass spectra of a) β-casein digest (1×10^{-7} M), b) a digest mixture of β-casein and BSA (1:25, molar ratio) and c) a diluted human serum sample treated without the γ-Fe_2O_3@$REVO_4$ affinity microspheres.

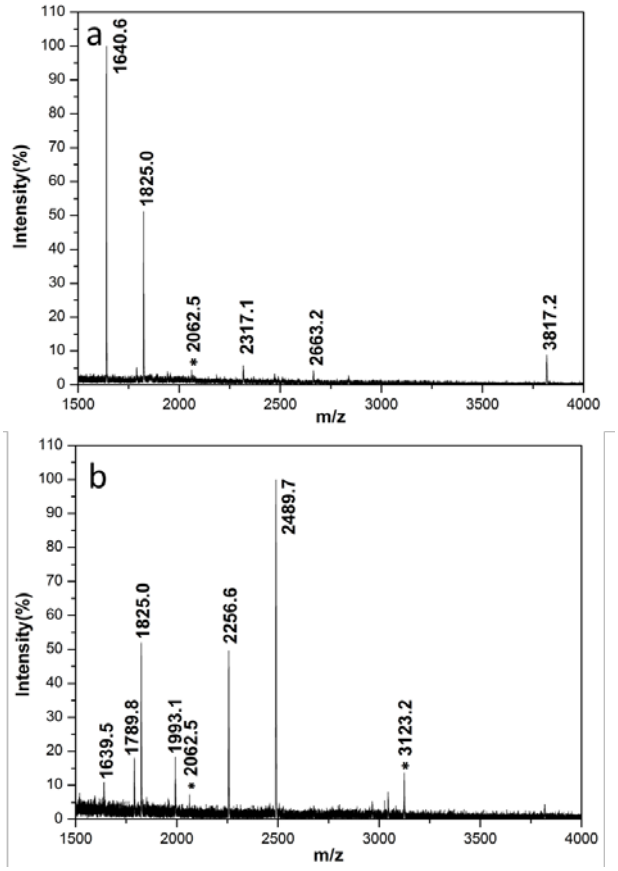

Fig. S6 MALDI-TOF mass spectra of a digest mixture of β-casein and BSA (1:25, molar ratio) treated with a) as-synthesized Fe_3O_4 and b) TiO_2 nanoparticles, respectively.

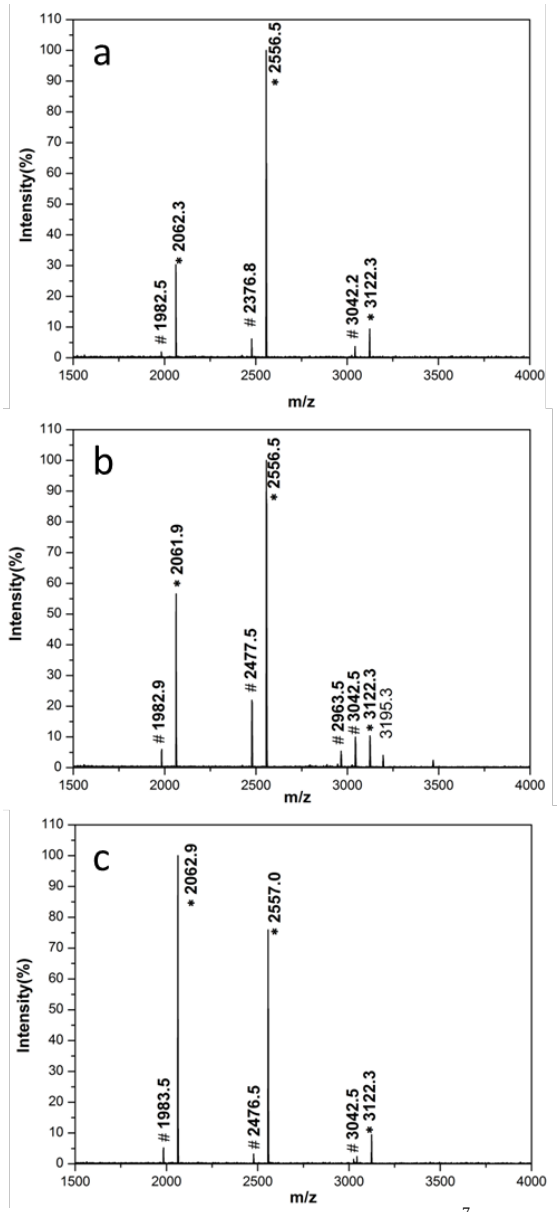

Fig. S7 MALDI-TOF mass spectra of the peptides from β-casein digest (1×10^{-7} M) treated with a) γ-Fe_2O_3@$SmVO_4$, b) γ-Fe_2O_3@$DyVO_4$, c) γ-Fe_2O_3@$HoVO_4$ microspheres respectively after these microspheres were recycled up to five times.

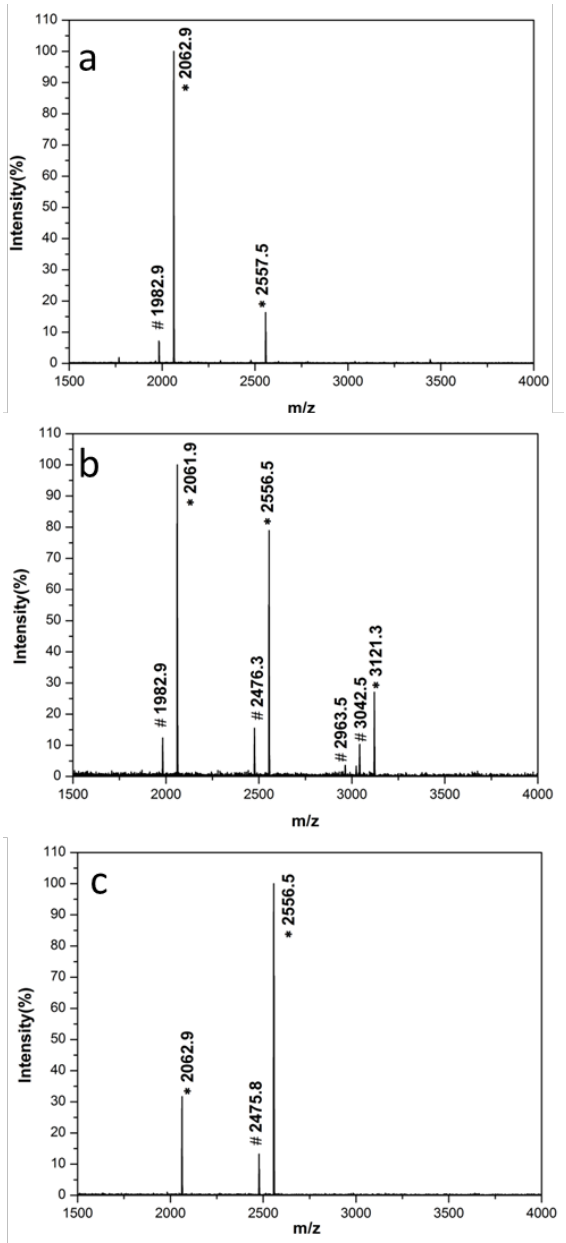

Fig. S8 MALDI-TOF mass spectra of the peptides from β-casein digest (1×10^{-7} M) treated with a) γ-Fe_2O_3@$SmVO_4$, b) γ-Fe_2O_3@$DyVO_4$, c) γ-Fe_2O_3@$HoVO_4$ microspheres respectively after these microspheres were recycled up to eight times.

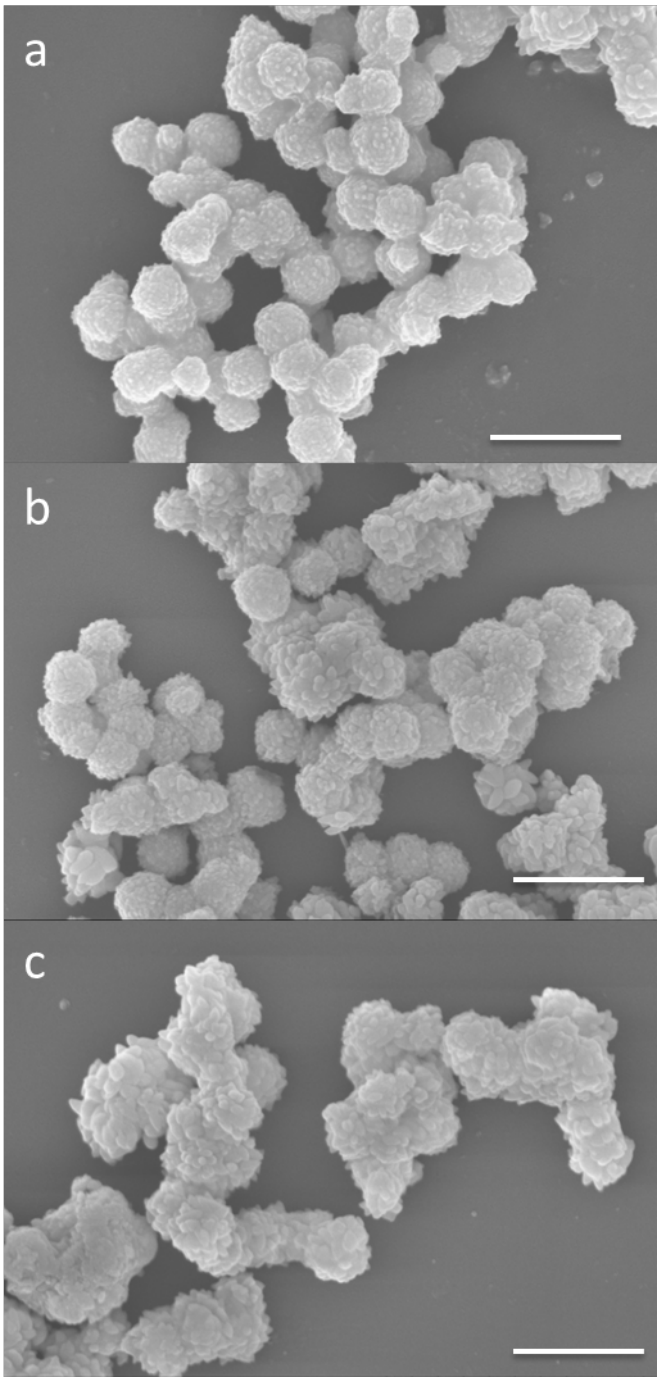

Fig. S9 SEM images of a) γ-Fe_2O_3@$SmVO_4$ b) γ-Fe_2O_3@$DyVO_4$ c) γ-Fe_2O_3@$HoVO_4$ after eight cycles using β-casein (1×10^{-7}) as analyte. Scale bar: 1 μm

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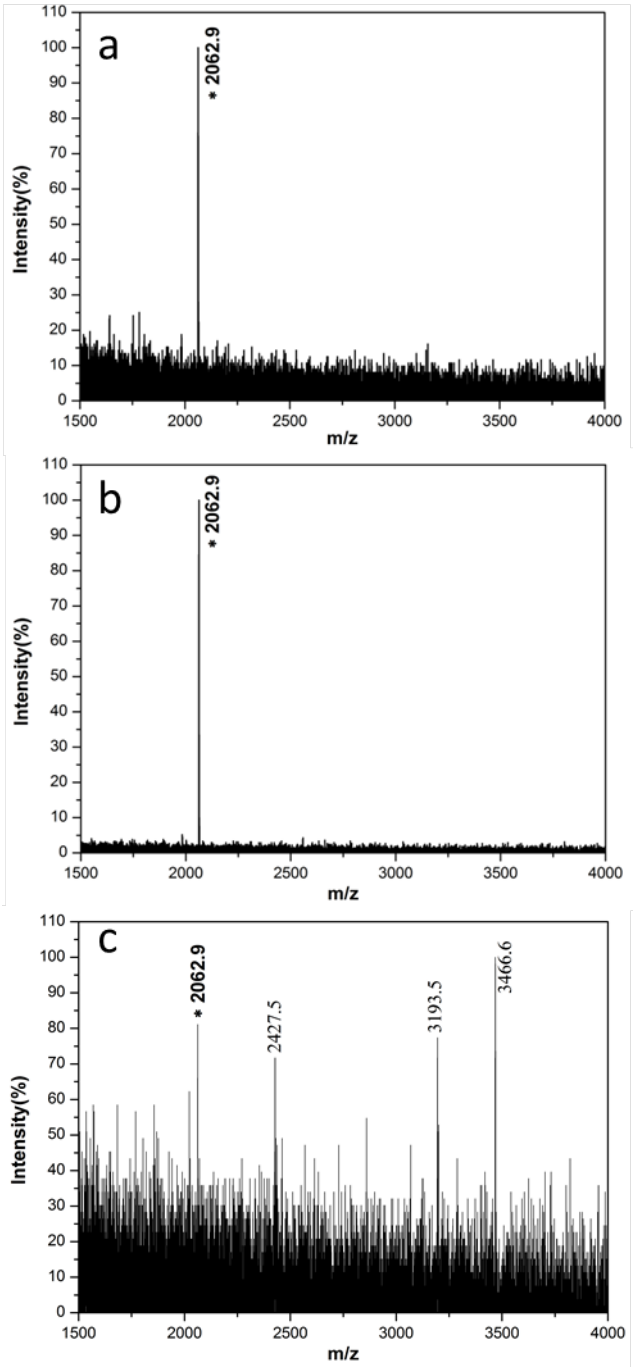

Fig. S10 MALDI-TOF mass spectra of the highly diluted β-casein digest (1×10^{-9}) treated with a) γ-Fe_2O_3@$SmVO_4$, b) γ-Fe_2O_3@$DyVO_4$, respectively, and c) MALDI-TOF mass spectra of the highly diluted β-casein digest (2×10^{-9}) treated with γ-Fe_2O_3@$HoVO_4$ microspheres.

Table S1. The phosphopeptides and their label signals identified by MALDI-TOF MS from tryptic digest of β-casein.

AA	Peptide sequences	Observed *m/z*	Theoretical *m/z*	Phosphorylation site
33-48	FQ[pS]EEQQQTEDELQDK	2061.3	2061.8	1
33-52	FQ[pS]EEQQQTEDELQDKIHPF	2555.5	2556.0	1
1-25	RELEELNVPGEIVE[pS]L[pS][pS][pS]EESITR	3121.6	3122.2	4

Table S2. Detailed Information of the Observed Endogenous Phosphopeptides from Human serum

NO.	Peptide sequences	Observed *m/z*	Theoretical *m/z*	Phosphorylation site
1	D[pS]GEGDFLAEGGGVR	1545.8	1545.5	1
2	AD[pS]GEGDFLAEGGGVR	1616.9	1616.7	1