

8 Electronic Supplementary Material

Supplementary data associated with this article can be found in the online version.

Electronic Supplementary Material S1

S1 Scanning electron microscopy (SEM) of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Yb}_2\text{O}_3$ performed on a JEOL, JSM-6010LV SEM. SEM pictures were taken in high vacuum mode at accelerating voltages of 10 kV and currents of 5–10 nA. Two different batches of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Yb}_2\text{O}_3$ were analyzed by energy dispersive X-ray spectroscopy for elemental analysis and revealed 3.0% and 2.2% (wt.%) ytterbium, respectively. The right SEM shows the polymer after grinding procedure.

Electronic Supplementary Material S2

S2 MALDI-TOF MS spectra of a digested protein mixture (α -casein, β -casein, myoglobin, cytochrome c, lysozyme, and bovine serum albumin) before (A) and after enrichment using $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Yb}_2\text{O}_3$ (B). Phosphopeptides are labelled with asterisks. **doubly charged phosphopeptide $[M+2H]^{2+} = 1561.1$ Da

Electronic Supplementary Material S3

S3 Overview of enriched phosphopeptides from digested α - and β -casein using Y(III) metal-loaded $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Yb}_2\text{O}_3$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Gd}_2\text{O}_3$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Nd}_2\text{O}_3$ and non-loaded $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Yb}_2\text{O}_3$

α -S1 and α -S2 represent the first and second subunits of α -casein, respectively. β -C represents peptides from β -casein.

“s” represents a phosphorylated serine in the peptide sequences

Electronic Supplementary Material S4

S4 Selectivity study for $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Yb}_2\text{O}_3$ using the synthetic phosphopeptide (VYGKTPSHLR $[M+H]^+ = 1140.20$) at different ratios; (a) 1:10, (b) 1:50, (c) 1:1000, (d) 1:5000, (e) 1: 10000, (f) 1:50000.

Electronic Supplementary Material S5

S5 MALDI-TOF MS spectra of the enriched synthetic phosphopeptide (VYGKTPSHLR $[M+H]^+ = 1140.20$) by $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Yb}_2\text{O}_3$ showing sensitivity down to the femtomolar range. The detection limit is dependent on the employed MALDI-TOF MS instrument.