Hollow fiber supported TiO₂ monolithic microextraction combined with capillary HPLC-ICP-MS for sensitive absolute quantification of phosphopeptides

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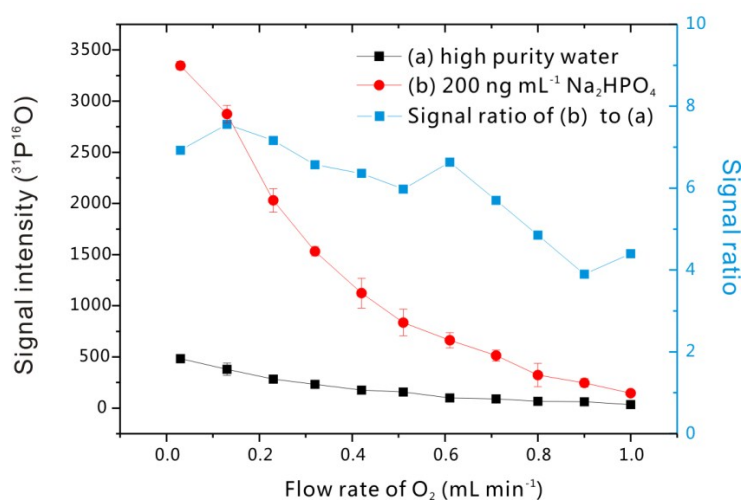**Supplementary materials**

Figure S1-S10

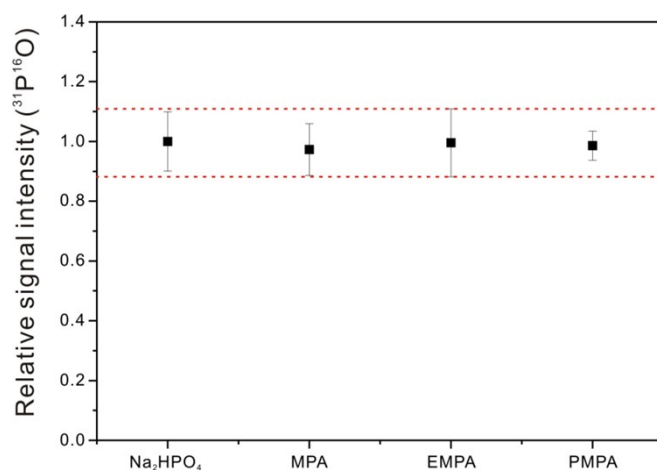**Fig. S1** Effect of the flow rate of added O_2 on the signal intensity of $^{31}P^{16}O$.

Fig. S2 ICP-CRC-MS response of Na_2HPO_4, MPA, EMPA and PMPA (c: 100 ng as P mL^{-1}).

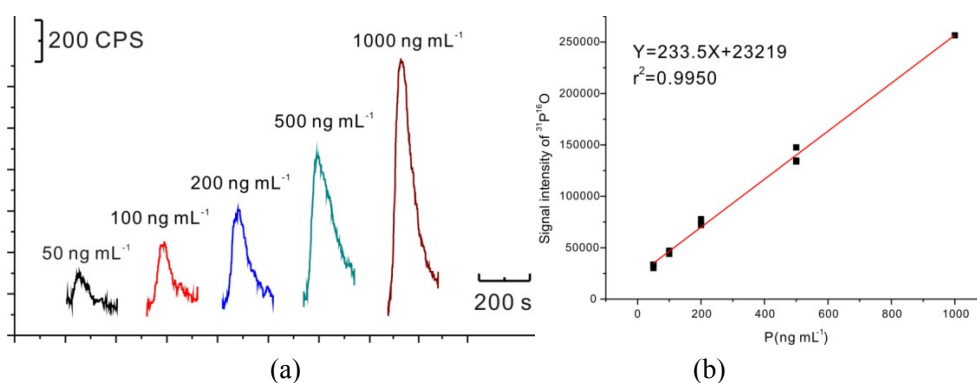|	
(a)	(b)

Fig. S3 Signal profile of Na_2HPO_4 at different concentrations obtained by capHPLC-ICP-CRC-MS (a) and the linear-fit curve (b).
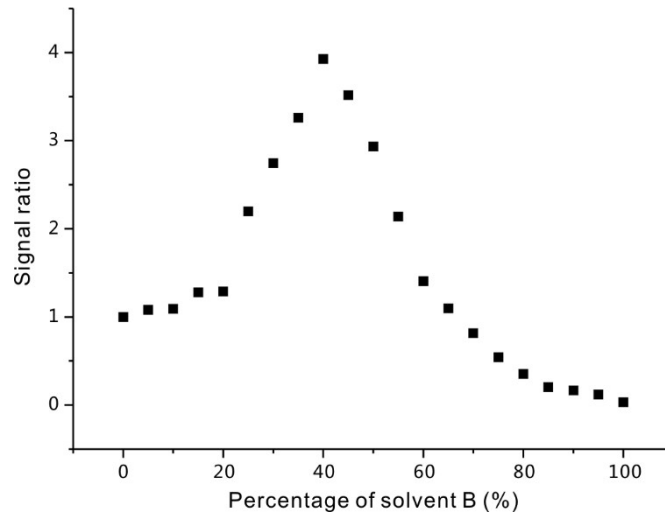
Fig. S4 Signal ratio of Na_2HPO_4 in mixed solvent A and B to that in solvent A obtained by capHPLC-ICP-CRC-MS. (solvent A: 0.1% (v/v) formic acid in water, solvent A: 0.1% (v/v) formic acid in acetonitrile)
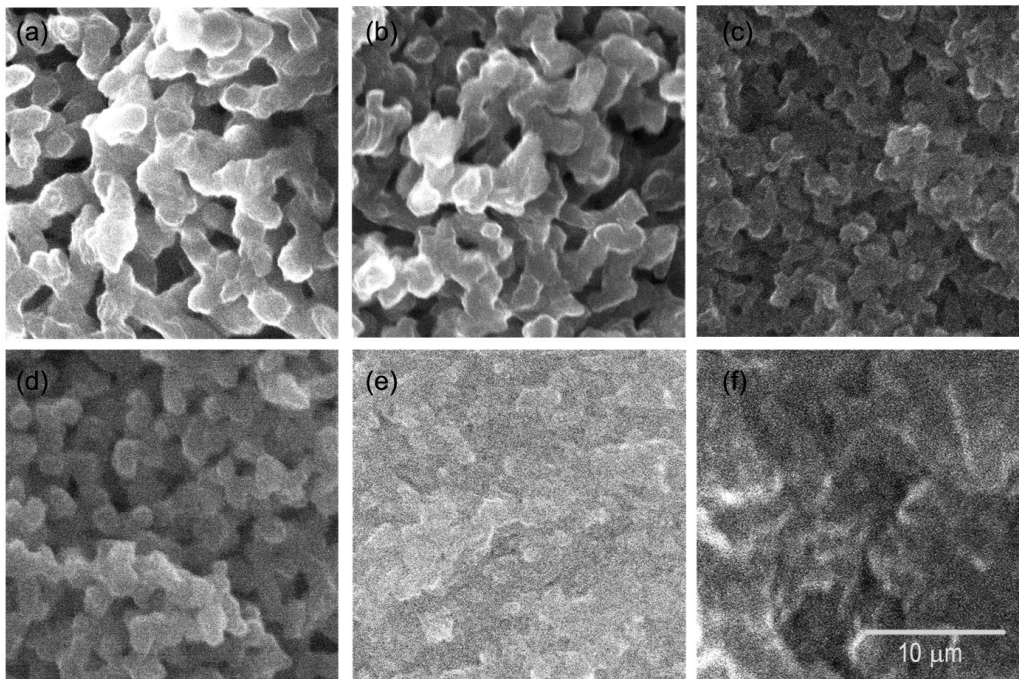

Fig. S5 Scanning electron micrographs (a)-(f) of TiO_2 monolith prepared by the method of No. 2, 3, 5, 6, 8 and 9, respectively.
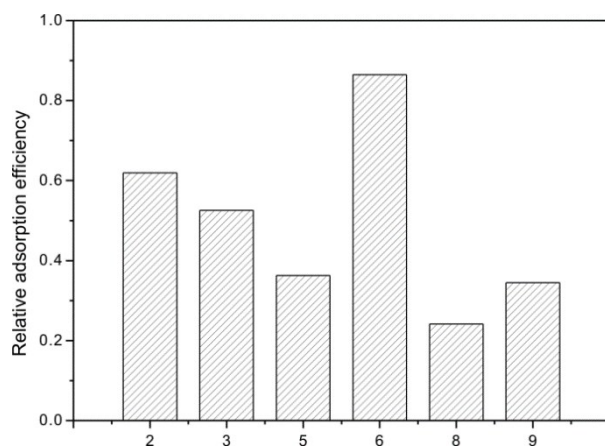
Fig. S6 Adsorption efficiency of β-casein peptide standards on different TiO$_2$ monoliths.
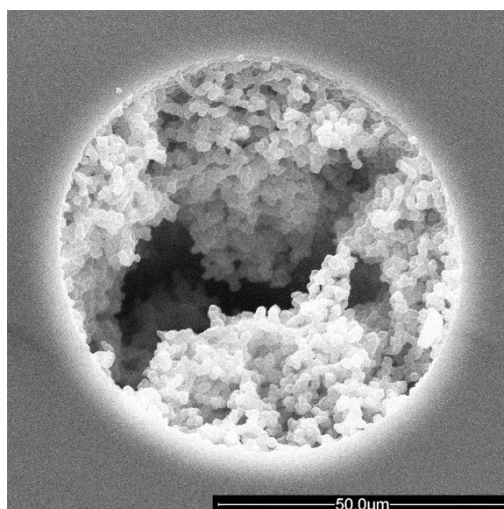

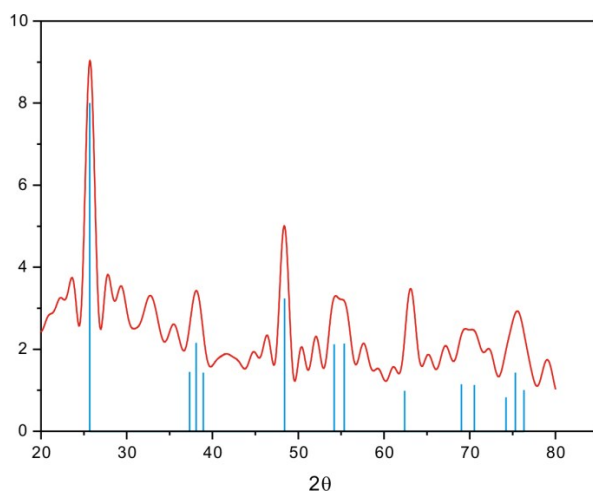**Fig. S7** Scanning electron micrograph of TiO$_2$ monolith prepared in fused silica capillary (50 μm i.d.).

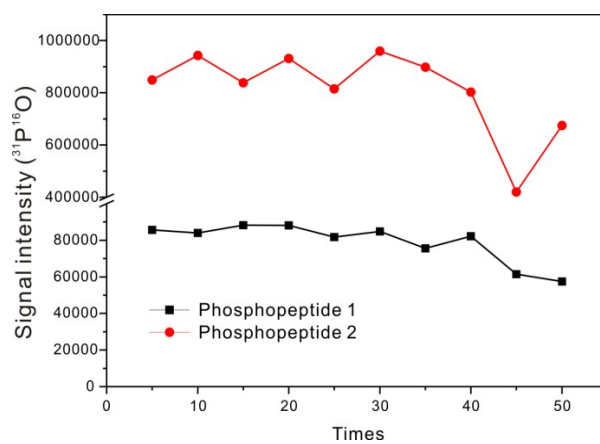**Fig. S8** XRD of HF-TiO$_2$ monolith. Blue line was the theoretical XRD pattern for anatase TiO$_2$.
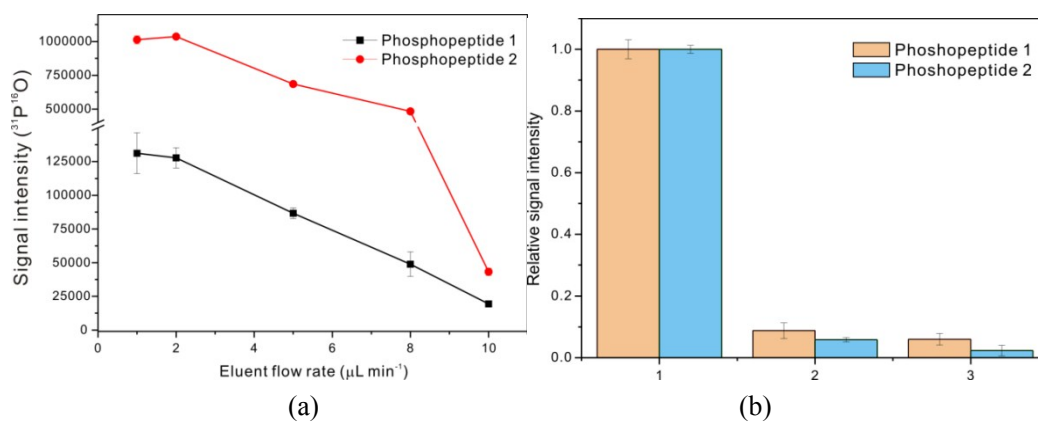
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Fig. S9 Lifespan of HF-TiO$_2$ monolith.

Fig. S10 Effect of eluent flow rate (a) and eluent volume (b) on the signal intensity of phosphopeptides by HF-TiO$_2$ monolithic microextraction-capHPLC-ICP-CRC-MS.