

Supporting Information

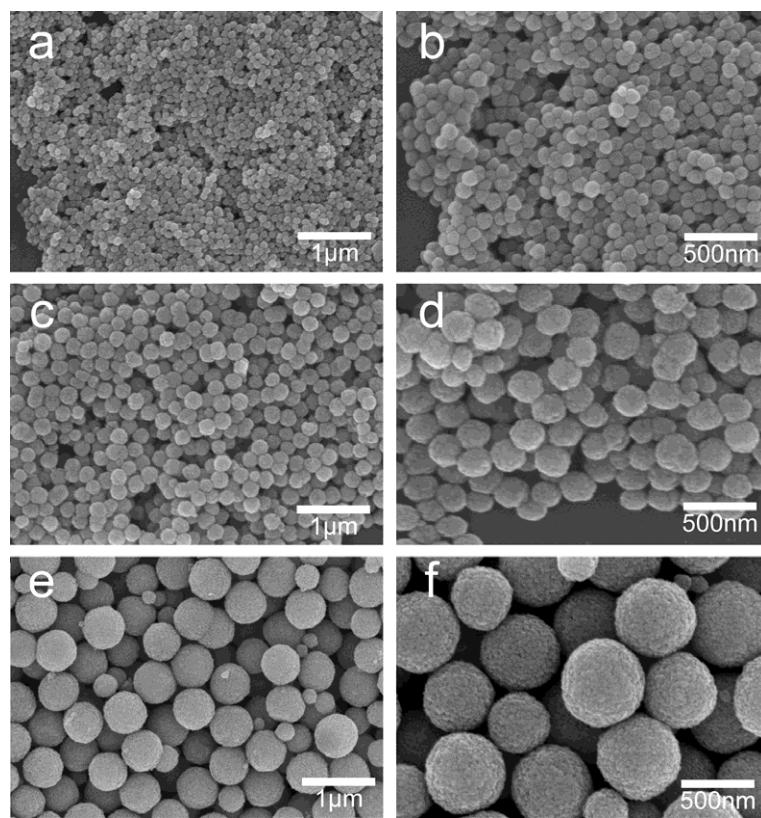


Fig. S1 SEM images of the precursor Fe_3O_4 particles with different size: 60 nm (a and b), 200 nm (c and d) and 500 nm (e and f).

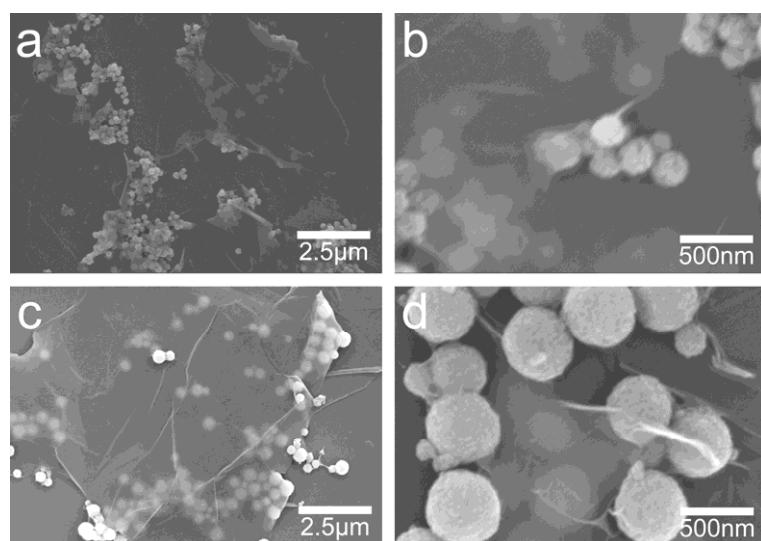


Fig. S2 SEM images of prepared GO- Fe_3O_4 with different precursor Fe_3O_4 particles: 200 nm (a and b) and 500 nm (c and d).

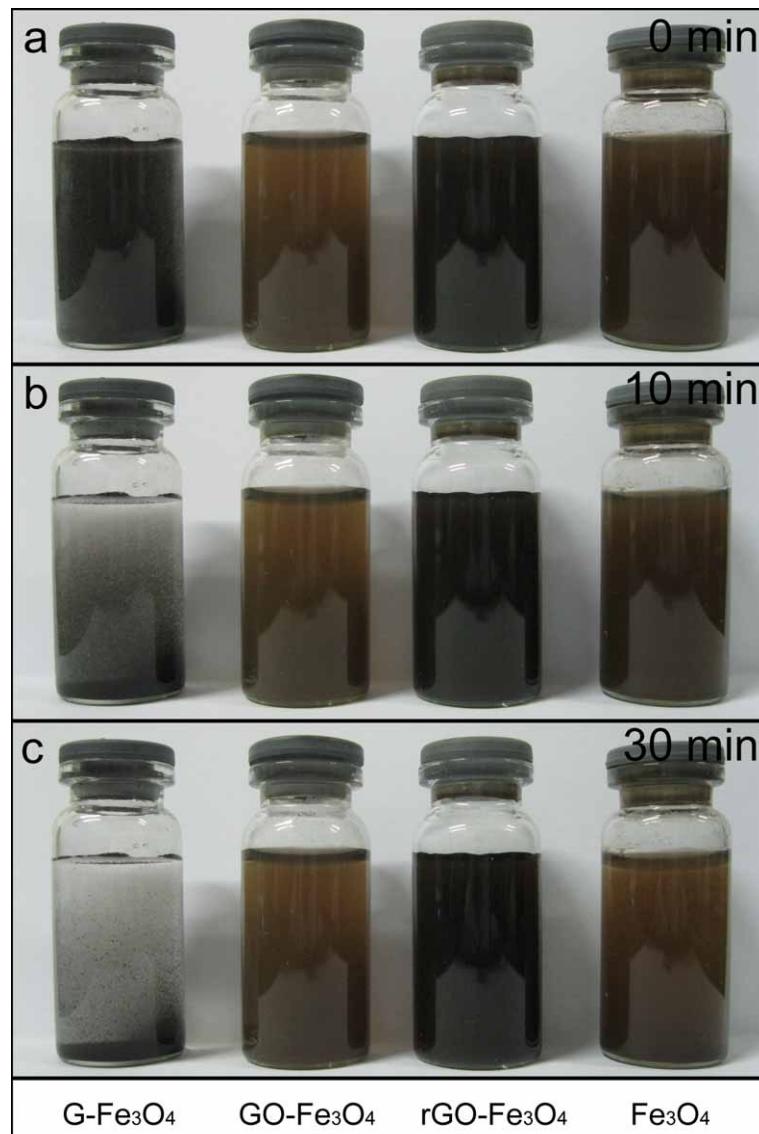


Fig. S3 Photos of the dispersion of graphene- Fe_3O_4 composites (G- Fe_3O_4) prepared using the solvothermal route, the dispersion of Fe_3O_4 particles, the dispersion of as-prepared GO- Fe_3O_4 composites and the dispersion of as-prepared GO- Fe_3O_4 composites.

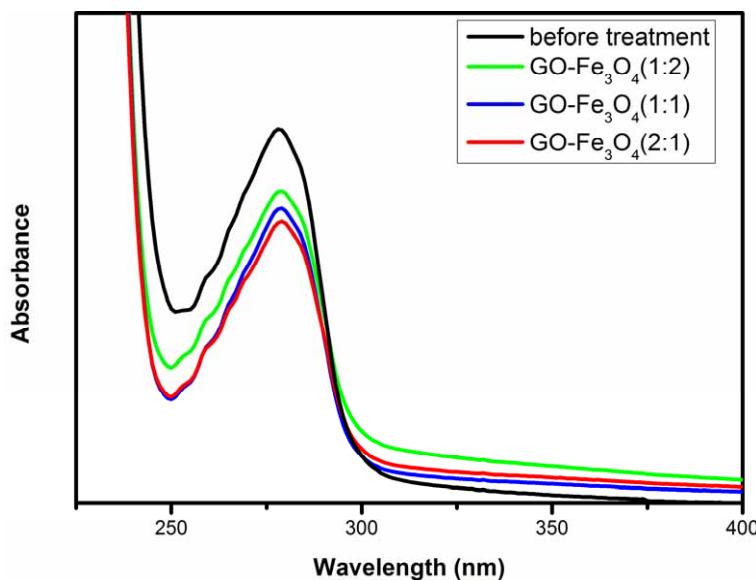


Fig. S4 Adsorption of BSA protein solution before and after treatment by GO-Fe₃O₄ composites with different ratios of GO to Fe₃O₄. The initial concentration of protein solution was 1 mg mL⁻¹ and the concentration of GO-Fe₃O₄ composites was 1 mg mL⁻¹.

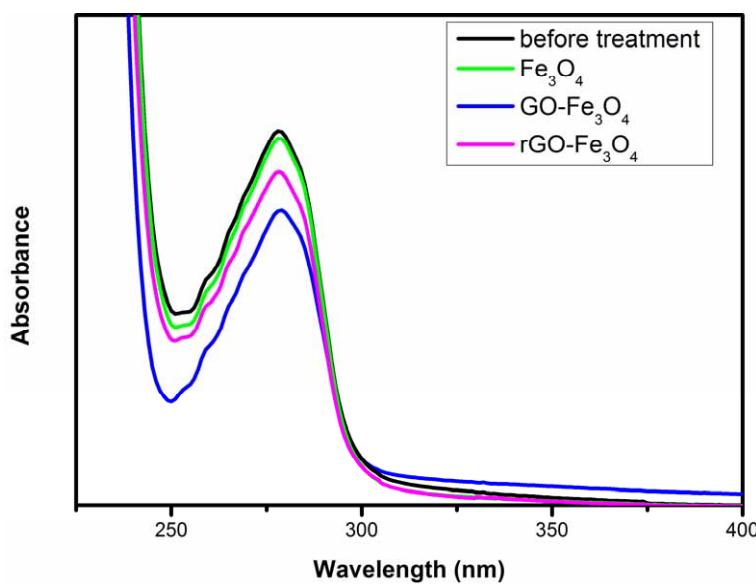


Fig. S5 Adsorption of BSA protein solution before and after treatment by Fe₃O₄ particles, GO-Fe₃O₄ and rGO-Fe₃O₄ composites. The initial concentration of protein solution was 1 mg mL⁻¹ and the concentration of Fe₃O₄ particles, GO-Fe₃O₄ and rGO-Fe₃O₄ composites was 1 mg mL⁻¹.

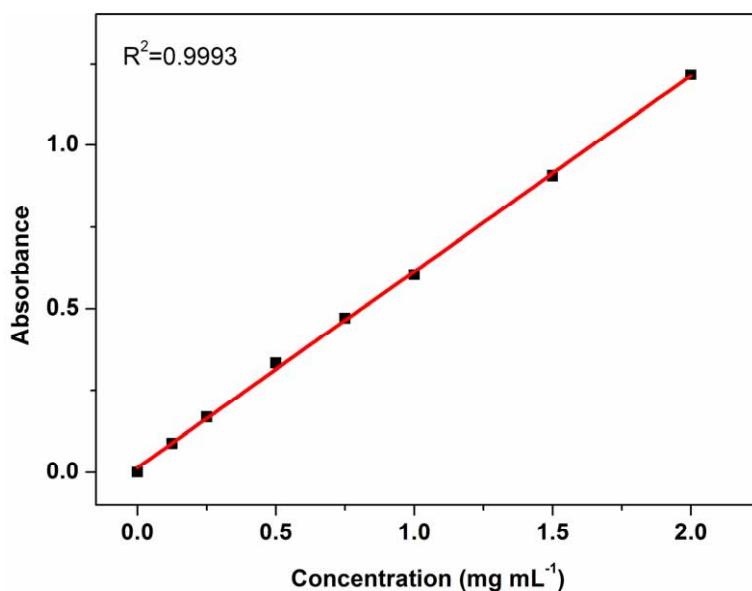


Fig. S6 Calibration curve of the absorbance at 280 nm versus the BSA concentrations.

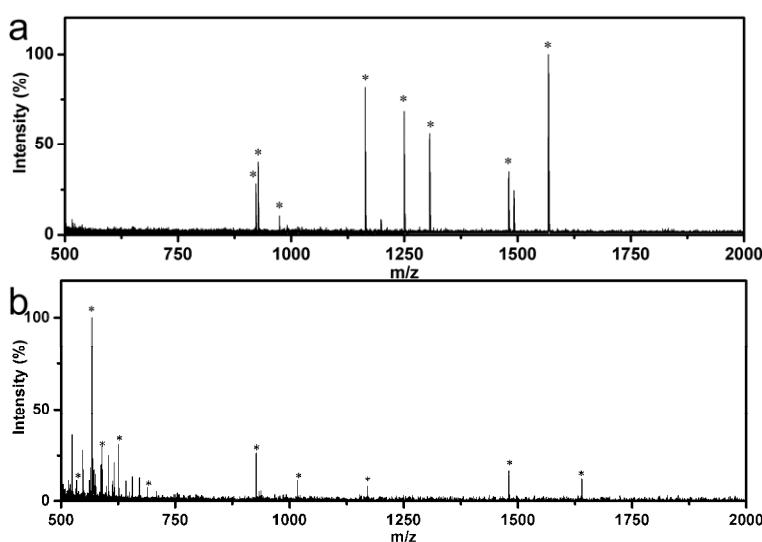


Fig. S7 MALDI-TOF mass spectra of the diluted digest of BSA ($5 \text{ fmol } \mu\text{L}^{-1}$) after enrichment using (a) the Fe_3O_4 particles and (b) commercial Zip-TipC18 pipette tip.

Table S1 The search results of the tryptic digest of BSA before and after enrichment by rGO- Fe₃O₄ hybrids, Zip-TipC18 pipette tip.

AA	Mr(calc)	Peptide sequences	None	Fe ₃ O ₄	rGO-Fe ₃ O ₄	ZipTipC18
24–28	655.3402	RRDTHKS			√	√
29–34	711.3664	KSEIAHRF			√	
35–44	1249.6000	RFKDLGEEHFKG		√		
37–44	973.4505	KDLGEEHFKG		√	√	
66–75	1162.6234	KLVNELTEFAKT		√	√	
152–156	589.3071	KADEKKF			√	√
157–160	536.2747	KFWGKY	√		√	√
161–167	926.4861	KYLYEIARR		√	√	√
223–228	648.3265	RCASIQKF	√		√	
229–232	507.2441	KFGERA			√	
233–241	1000.5818	RALKAWSVARL			√	
236–241	688.3656	KAWSVARL			√	√
249–256	921.4807	KAEFVEVTKL		√	√	
310–318	1014.4804	KSHCIAEVEKD			√	√
347–359	1567.7000	KDAFLGSFLYEYSRR		√		
402–412	1304.7088	KHLVDEPQNLIKQ		√	√	
421–433	1478.7881	KLGEYGFQNALIVRY		√	√	√
434–437	566.3176	RYTRKV	√		√	√
437–451	1638.9305	RKVPQVSTPTLVEVSRS			√	√
499–507	1023.4477	KCCTESLVNRR			√	
549–557	1013.6121	KQTALVELLKHK			√	
Peptides matched			3	8	19	9
Sequence coverage (%)			-	11	21	11