Supporting information for

Poly(acrylic acid)-*block*-poly(vinyl alcohol) Anchored Maghemite Nanoparticles Designed for Multi-stimuli Triggered Drug Release

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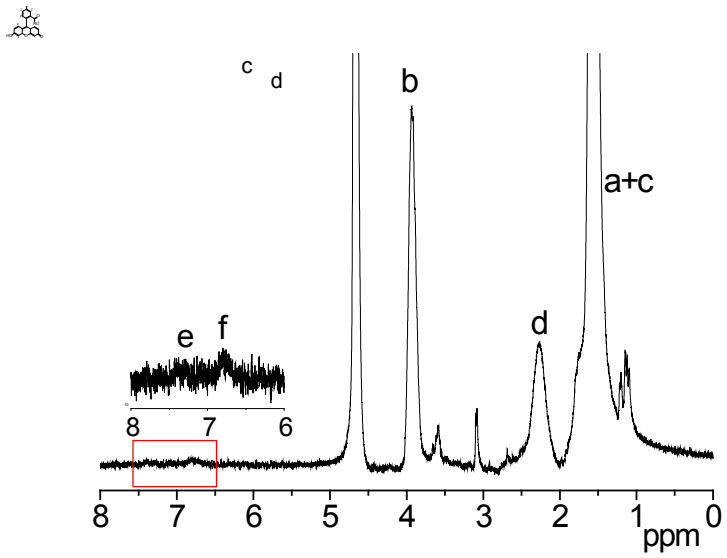

Figure S1. ^{1}H NMR spectrum of FA-labelled PVOH-*b*-PAA copolymer, insert: the partially enlarged spectra in the range of 6 ~ 8 ppm, and assignment of the protons; a grafting degree of *ca*. 1.4 *mol.* % (PAA-FA blocks out of overall PAA blocks) was confirmed. The spectrum was recorded in D_2O at room temperature with a 250 MHz Bruker spectrometer.

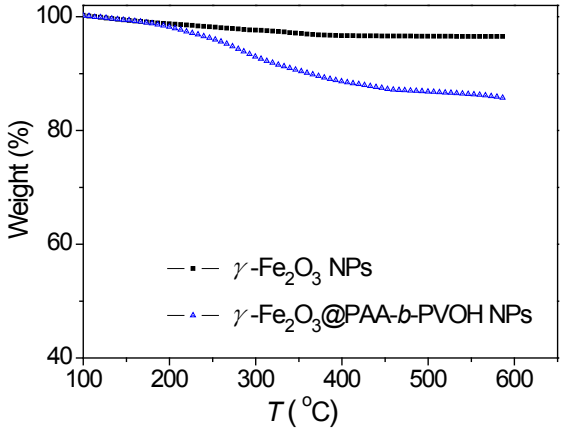

Figure S2. TGA traces of the γ-Fe_2O_3 nanoparticles before and after coating with PAA-*b*-PVOH macromolecules, and a polymer fraction of 12 *wt*.% was estimated. Experiments were performed from 20 to 600°C at a heating rate of 20°C/min under air with a TA Q100 Instrument.

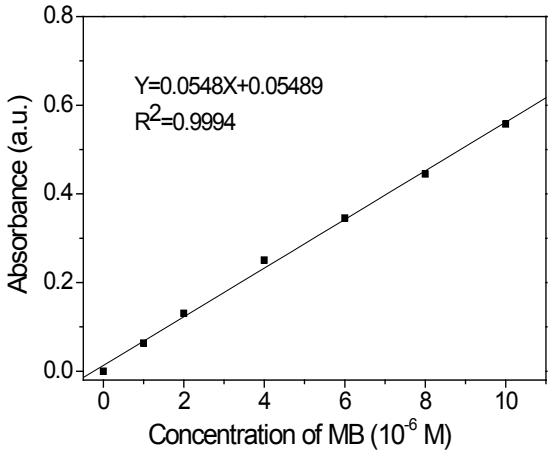

Figure S3. Calibration curve: methylene blue (MB) absorbance at 665 nm as a function of concentration. A good linear fitting was observed with $R^2 = 0.9994$.

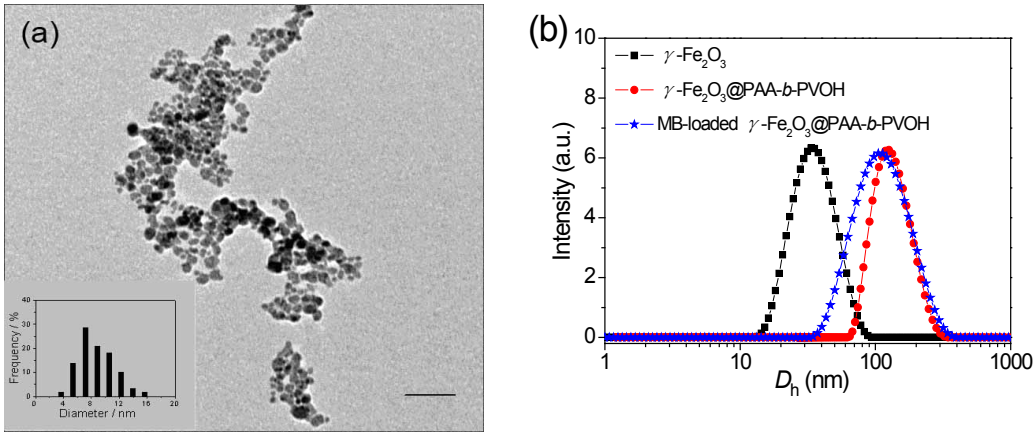

Figure S4. (a) TEM image of the γ-Fe_2O_3 NPs (scale bar: 50 nm) (insert: statistical size distribution histogram from *ca*. 200 particles), and (b) size distribution of the bare γ-Fe_2O_3, γ-Fe_2O_3@PAA-*b*-PVOH and γ-Fe_2O_3@PAA-*b*-PVOH@MB NPs suspension as determined by DLS.

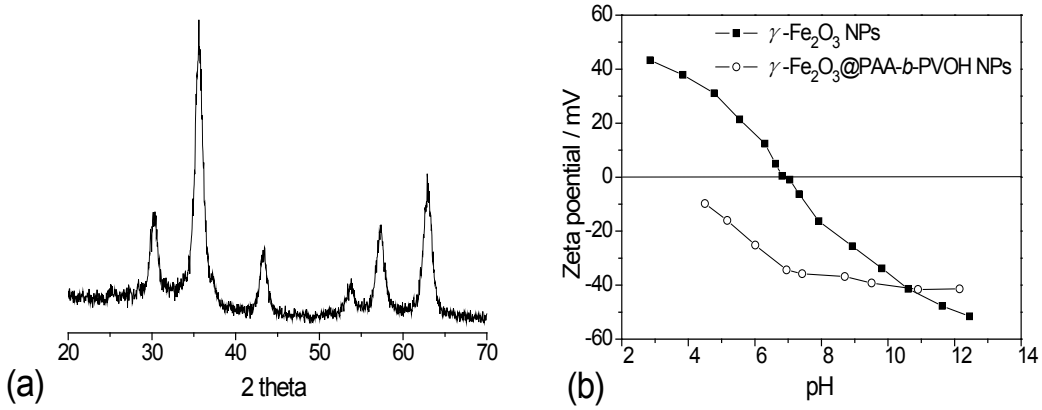

Figure S5. (a) XRD patterns of the γ-Fe_2O_3@PAA-*b*-PVOH NPs and (b) evolution of zeta potential *vs.* pH for the bare γ-Fe_2O_3 NPs (the solid lines just serve to guide the eye). X-ray diffraction was performed on a Philips PW1700 diffractometer with CuKα radiation (λ = 1.5418 Å).

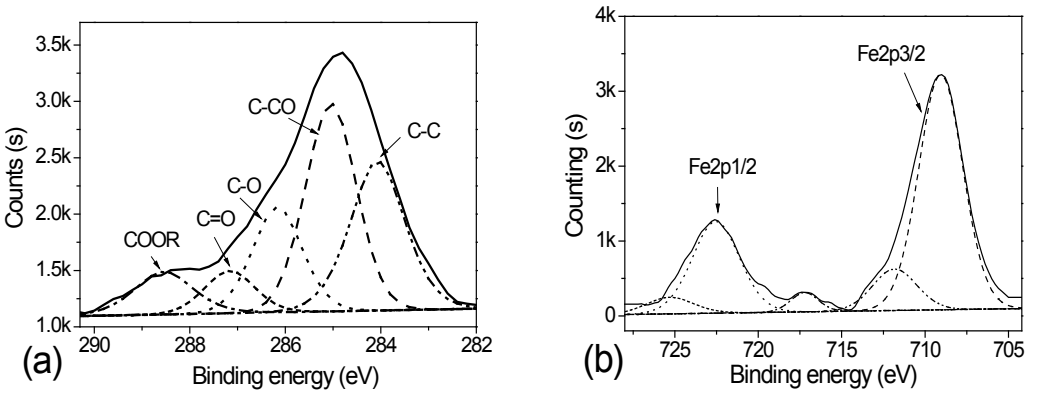

Figure S6. XPS spectra of the γ-Fe_2O_3@PAA-*b*-PVOH NPs: fitted C 1s (a) and Fe 2p spectra (b). The C1s XPS spectrum (a) of the γ-Fe_2O_3@PAA-*b*-PVOH NPs can be fitted into 5 component peaks centered at 288.6, 287.2 and 286.2, 285.1 and 284.0 eV, representing the carbon atoms of COOR, C=O, C-O, C-CO and C-C units, respectively.[1] And the C1s peak (COOR) strongly supports the presence of the PAA-*b*-PVOH copolymer. Peaks at 709.1 (Fe 2p3/2) and 722.6 eV (Fe 2p1/2) were also observed for iron oxides components (b). In addition, weak satellite peak (717.2 eV) on their high binding energy side was also observed. Such a spectrum is typical of iron oxides (α- and γ-Fe_2O_3 polymorphs).[2] XPS experiments were performed with a VG Scientific 220 i-XL ESCALAB spectrometer, equipped with a non-monochromatised MgKα source (hv = 1253,6 eV) at 100 W (10 kV and 10 mA). A pressure of 10^{-7} Pa was maintained in the chamber during analysis. The analysed area was *ca*. 150 µm in diameter. The full spectra (0 ~ 1150 eV) were obtained with constant pass energy of 150 eV and high-resolution spectra at constant pass energy of 40 eV. Charge neutralization was required for insulating samples. The peaks were referenced to C1s peak at 284.7 eV. High-resolution spectra were fitted using the AVANTAGE software provided by ThermoFisher Scientific.

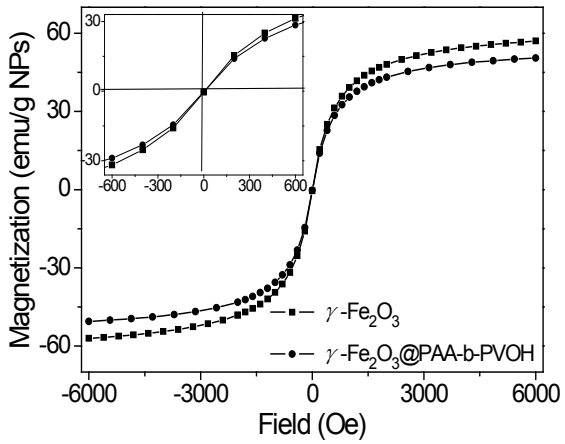

Figure S7. SQUID curves of the γ-Fe_2O_3@PAA-*b*-PVOH NPs and bare γ-Fe_2O_3 NPs at 300 K (insert: magnified SQUID curves in the range of -600 to 600 Oe).

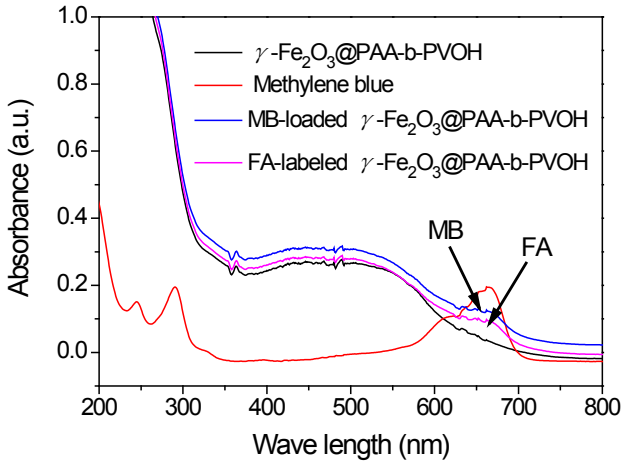

Figure S8. UV/*vis* spectra of the γ-Fe_2O_3@PAA-*b*-PVOH NPs, pure methylene blue, γ-Fe_2O_3@PAA-*b*-PVOH@MB NPs and FA-labeled γ-Fe_2O_3@PAA-*b*-PVOH NPs

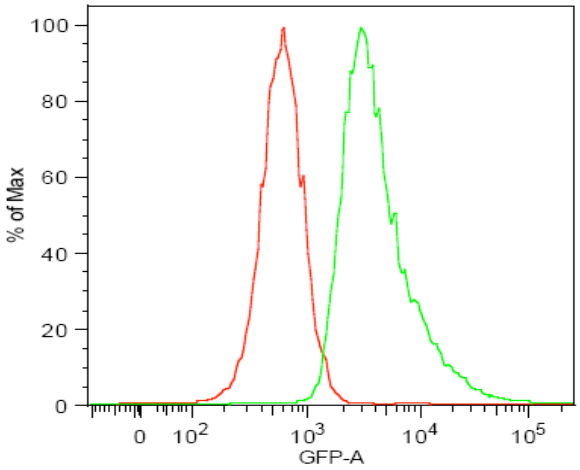

Figure S9. FACS measurement of untreated MEL-5 cells (red) and cells after incubation with FA-labelled γ-Fe_2O_3@PAA-*b*-PVOH NPs (50 µg/mL, 3-h incubation, green), and plotting log of FITC intensity (GFP-A on *x*-axis) against the number of cells (counts on *y*-axis)

References

1.K. Hayashi, K. Ono, H. Suzuki, M. Sawada, M. Moriya, W. Sakamoto and T. Yogo, *Acs Appl Mater Inter*, 2010, 2, 1903-1911.

2.S. S. Huang, Y. Fan, Z. Y. Cheng, D. Y. Kong, P. P. Yang, Z. W. Quan, C. M. Zhang and J. Lin, *J Phys Chem C*, 2009, 113, 1775-1784.