# Design of Yolk-shell Fe$_3$O$_4$@PMAA Composite Microspheres for Adsorption of Metal Ions and pH-controlled Drug Delivery

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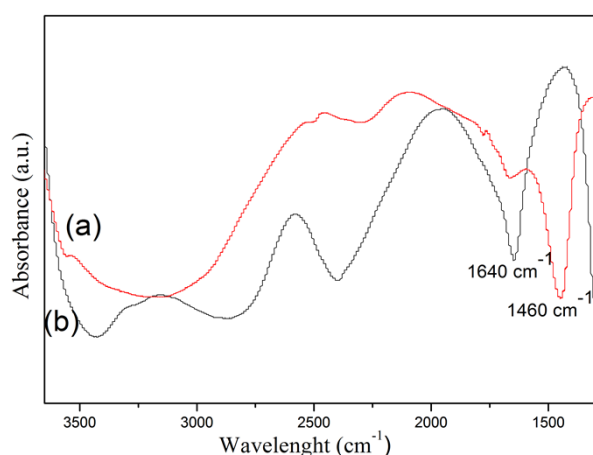
Fig. S1. FTIR spectra of Fe$_3$O$_4$@PMAA microspheres in a different phosphate buffer solution: (a) pH=4.5, (b) pH=10. The absorption peak at 2300-2400 cm^{-1} is attributed to the dihydric phosphate.[1]
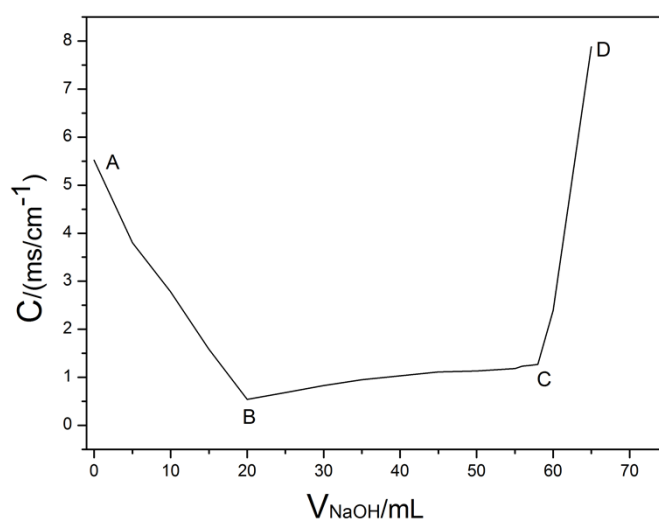

Fig. S2 Conductivity titration curve of yolk-shell Fe$_3$O$_4$/PMAA microspheres (the shell thickness is 40 nm) dispersed in HCl aqueous solution by 0.01 mol L^{-1} NaOH titrant

As shown in Fig. S2, when 0.01 mol L^{-1} NaOH titrant (the exact concentration is 0.0104 mol L^{-1} after the calibration of potassium hydrogen phthalate) was added dropwise into the Fe$_3$O$_4$@PMAA microspheres dispersed in 0.01 mol L^{-1} HCl aqueous solution, the electric conductivity of the dispersion first decreased abruptly due to the formation of Na$^+$ ions instead of H$^+$ ions during the neutralization reaction between NaOH and HCl (the electric conductivity of H$^+$ is larger than that of Na$^+$). As the electric conductivity of the dispersion decreased to minimum value (point B), it suggested that the HCl had completely reacted with NaOH. And then the electric conductivity of the dispersion increased slowly, because the neutralization reaction of the –COOH groups and the NaOH led to the increasing Na$^+$ concentration and the formation of –COO$^-$ (their electric conductivities are weak). At point C, the injected NaOH solution entirely reacted with –COOH groups. After that, the electric conductivity of the dispersion increased abruptly due to the increasing NaOH concentration (the electric conductivity of OH$^-$ is large). Therefore, the content of –COOH groups in Fe$_3$O$_4$@PMAA microspheres (C$_{COOH}$, mmol g^{-1}) can be calculated by the following equation:

$$C_{COOH} = \frac{(V_C - V_B) \times C_{NaOH}}{M}$$

Where, V$_C$ is the volume of NaOH at point C (ml), V$_B$ is the volume of NaOH at point B (ml), C$_{NaOH}$ is the concentration of NaOH (mol L^{-1}) and M is the weight of Fe$_3$O$_4$@PMAA microspheres (g). Therefore, we can calculate from Fig. S2 that C$_{COOH}$ = (58.2-20.6)×0.0104/0.1 = 3.91 mmol g^{-1} for Fe$_3$O$_4$@PMAA-3.
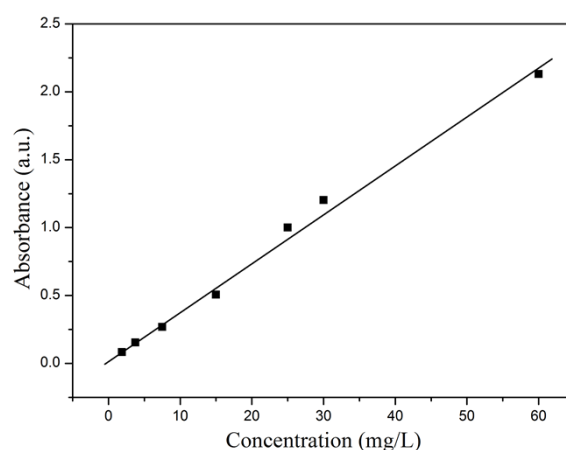
Fig. S3. Calibration curve of the absorbance at 272 nm *versus* the concentration of ceftriaxone sodium (CTX) solution
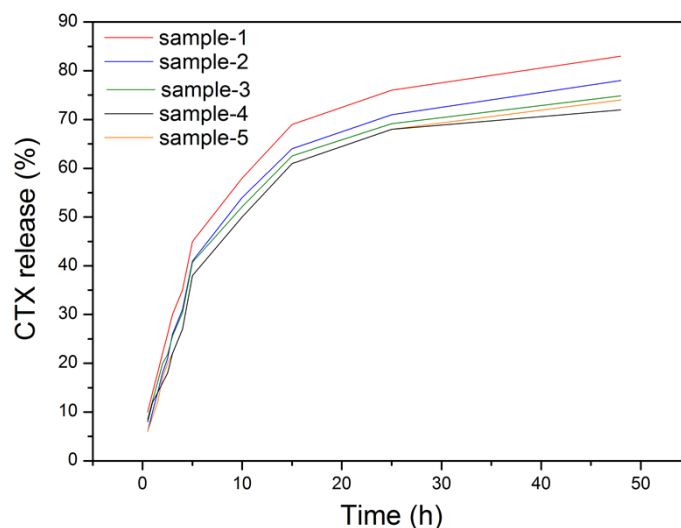
Fig. S4 The effect of thickness of PMAA shells and void space of yolk-shell $Fe_3O_4@PMAA$ microspheres on the release of CTX at pH=4.5.

Table S1 The influence of the thickness of PMAA shells and void space of yolk-shell $Fe_3O_4@PMAA$ microspheres on adsorption capacities of Pb^{2+} at pH 6 and drug loading capacity.

Sample	PMAA (nm)	Void space (μm^3)	q_e (mmol/g)	DLC (%)
$Fe_3O_4@PMAA$-1	15	0.13	1.02	94
$Fe_3O_4@PMAA$-2	25	0.13	1.87	138
$Fe_3O_4@PMAA$-3	40	0.13	2.48	180
$Fe_3O_4@PMAA$-4	40	0.058	2.45	178
$Fe_3O_4@PMAA$-5	40	0.024	1.98	152

Notes and references

1. F. Loretta, S. Perumal and S. Ramalingom, *Asian. Chemistry*, 2013, **25**, 1921.