**SUPPOTING INFORMATION**

**Dual Shelled Fe\(_3\)O\(_4\)/Polydopamine Hollow Microspheres As An Effective Eu(III) Absorber**

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**Preparation of the Fe\(_3\)O\(_4\)@PDA nanospheres based on 120 nm Fe\(_3\)O\(_4\) nanospheres:**

Typically, FeCl\(_3\)·6H\(_2\)O (2 mmol), NaOAc (1.5 g) and PAA (0.5 g) was dissolved in EG in a beaker. After vigorous stirring, the obtained homogeneous solution was transferred to a Teflon-lined stainless-steel autoclave and then sealed to heat at 200 °C. After a 10 h reaction period, the autoclave was cooled to room temperature. The obtained Fe\(_3\)O\(_4\) nanospheres were washed with water and ethanol for 3 times and then dried in a vacuum oven over night.

The following PDA coating was similar to the preparation of hollow Fe\(_3\)O\(_4\)@PDA nanospheres. Firstly, the Fe\(_3\)O\(_4\) nanospheres (10 mg) were thoroughly dispersed within 40 mL C\(_2\)H\(_5\)OH. 1 h later, 40 mL DA in PBS (0.1 g/L) was added into the above
solution. Then, the reaction was conducted under sonication for 3 h. Finally, the product was magnetically separated from the solution after the reaction. The residues were washed with water and ethanol, and then dried in vacuum to form a black powder.

**Preparation of the Fe$_3$O$_4$@PDA microspheres based on 300 nm Fe$_3$O$_4$ microspheres:**

FeCl$_3$·6H$_2$O (2 mmol), NaOAc (1.5 g) and NaAcrylate (1.5 g) was dissolved in EG in a beaker. After vigorous stirring, the obtained homogeneous solution was transferred to a Teflon-lined stainless-steel autoclave and then sealed to heat at 200 °C. After a 10 h reaction period, the autoclave was cooled to room temperature. The obtained Fe$_3$O$_4$ microspheres were washed with water and ethanol for 3 times and then dried in a vacuum oven over night.

The following PDA coating was similar to the preparation of hollow Fe$_3$O$_4$@PDA microspheres. Firstly, the Fe$_3$O$_4$ microspheres (20 mg) were thoroughly dispersed within 40 mL C$_2$H$_5$OH. 1 h later, 40 mL DA in PBS (0.25 g/L) was added into the above solution. Then, the reaction was conducted under sonication for 3 h. Finally, the product was magnetically separated from the solution after the reaction. The residues were washed with water and ethanol, and then dried in vacuum to form a black powder.

**Preparation of the β-FeOOH@PDA nanorods:**

FeCl$_3$ (4 mmol) and PVP (1 g) were dissolved in double distilled water (40 mL) and magnetically stirred to form a homogeneous solution. After 30 min, it was transferred into a Teflon-lined stainless steel autoclave, kept at 100 °C for 12 h and then cooled to room temperature on standing. The resultant β-FeOOH particles were rinsed successively with water and ethanol.

The following PDA coating was similar to the preparation of hollow Fe$_3$O$_4$@PDA nanospheres. Firstly, the β-FeOOH particles (20 mg) were thoroughly dispersed within 40 mL C$_2$H$_5$OH. 1 h later, 40 mL DA in PBS (0.1 g/L) was added into the above solution. Then, the reaction was conducted under sonication for 3 h. Finally, the product was magnetically separated from the solution after the reaction. The residues were
washed with water and ethanol, and then dried in vacuum to form a black powder.

Preparation of the porous Fe$_3$O$_4$@PDA nanospheres based on the 100 nm porous Fe$_3$O$_4$ nanospheres:

FeCl$_3$·6H$_2$O (2 mmol) was dissolved in a mixture of EG and DEG (V$_{EG}$/V$_{DEG}$ = 5/15, total volume is 20 mL) in a beaker under magnetic stirring. After 30 min, 2 g of PVP was added to the above solution and the suspension was heated at 120 °C to give a transparent solution. After an hour, 1.5 g NaOAc was added into the above solution and stop heating. After vigorous stirring for further 30 min, the obtained homogeneous solution was transferred to a Teflon-lined stainless-steel autoclave (25 mL volume) and then sealed to heat at 200 °C. After a 12 h reaction period, the autoclave was cooled to room temperature. The obtained porous Fe$_3$O$_4$ nanospheres were washed 3 times with ethanol and water, and then dried in vacuum for 12 h.

The following PDA coating was similar to the preparation of hollow Fe$_3$O$_4$@PDA nanospheres. Firstly, the porous Fe$_3$O$_4$ nanospheres (20 mg) were thoroughly dispersed within 40 mL C$_2$H$_5$OH. 1 h later, 40 mL DA in PBS (0.25 g/L) was added into the above solution. Then, the reaction was conducted under sonication for 3 h. Finally, the product was magnetically separated from the solution after the reaction. The residues were washed with water and ethanol, and then dried in vacuum to form a black powder.

**Fig. S1** Low magnification SEM images of the 260 nm Fe$_3$O$_4$ hollow spheres (left) and 360 nm dual-shelled Fe$_3$O$_4$@PDA hollow spheres prepared under the DA concentration of 4.4 mM (right).
**Fig. S2** TEM images of the pristine Fe$_3$O$_4$ hollow spheres with average size of 260 nm.

**Fig. S3** TEM images of the single dual-shelled Fe$_3$O$_4$@PDA hollow spheres with different shell thickness 20 nm.

**Fig. S4** TEM images of the dual-shelled Fe$_3$O$_4$@PDA hollow spheres (based on 120 nm nanospheres, DA concentration: 0.4 mM) with different magnification.

**Fig. S5** TEM images of the dual-shelled Fe$_3$O$_4$@PDA hollow nanospheres (based on 120
nm nanospheres, DA concentration: 0.7 mM) with different magnification.

Fig. S6 TEM images of the dual-shelled Fe₃O₄@PDA hollow nanospheres (based on 120 nm microspheres, DA concentration: 1 mM) under the 4 h reaction.

Fig. S7 TEM images of the Fe₃O₄@PDA core/shell spheres (based on 300 nm microspheres) with different magnification.
**Fig. S8** TEM images of the Fe₃O₄@PDA core/shell spheres (based on 100 nm porous nanospheres) with different magnification.

**Fig. S9** Barrett–Joyner–Halenda (BJH) pore size distribution plot of 260 nm hollow Fe₃O₄ microspheres and 300 nm Fe₃O₄@PDA particles with shell thickness of 20 nm.
Fig. S10 Distribution of Eu(III) species as a function of solution pH values.