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## SUPPOTING INFORMATION

# Dual Shelled $Fe_3O_4$/Polydopamine Hollow Microspheres As An Effective Eu(III) Absorber

*Qunling Fang[1a], Shengxia Duan[1b], JianfengZhang[a], Jiaxing Li[b,d]*, Ken Cham-Fai Leung[c]**

[a]*School of Medical Engineering, Hefei University of Technology, Hefei, 230009, P.R. China*
[b]*Key Laboratory of Novel Thin Film Solar Cells, Institute of Plasma Physics, Chinese Academy of Sciences, P.O. Box 1126, Hefei 230031, P.R. China*
[c]*Department of Chemistry, Hong Kong Baptist University, Kowloon, Hong Kong SAR, P. R. China*
[d] *Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, P.R. China*

***Corresponding authors:**

*Jiaxing Li*
E-mail: lijx@ipp.ac.cn

*Ken Cham-Fai Leung*
Email: cfleung@hkbu.edu.hk

[1] *The two authors contributed equally to this work*

### Preparation of the $Fe_3O_4$@PDA nanospheres based on 120 nm $Fe_3O_4$ nanospheres:

Typically, $FeCl_3 \cdot 6H_2O$ (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 $Fe_3O_4$ 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 $Fe_3O_4$@PDA nanospheres. Firstly, the $Fe_3O_4$ nanospheres (10 mg) were thoroughly dispersed within 40 mL $C_2H_5OH$. 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 $Fe_3O_4$@PDA microspheres based on 300 nm $Fe_3O_4$ microspheres:**

$FeCl_3 \cdot 6H_2O$ (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 $Fe_3O_4$ 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 $Fe_3O_4$@PDA microspheres. Firstly, the $Fe_3O_4$ microspheres (20 mg) were thoroughly dispersed within 40 mL $C_2H_5OH$. 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 $Fe_3O_4$@PDA nanospheres. Firstly, the β-FeOOH particles (20 mg) were thoroughly dispersed within 40 mL $C_2H_5OH$. 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 $Fe_3O_4$@PDA nanospheres based on the 100 nm porous $Fe_3O_4$ nanospheres:**

$FeCl_3 \cdot 6H_2O$ (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 $Fe_3O_4$ 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 $Fe_3O_4$@PDA nanospheres. Firstly, the porous $Fe_3O_4$ nanospheres (20 mg) were thoroughly dispersed within 40 mL $C_2H_5OH$. 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.

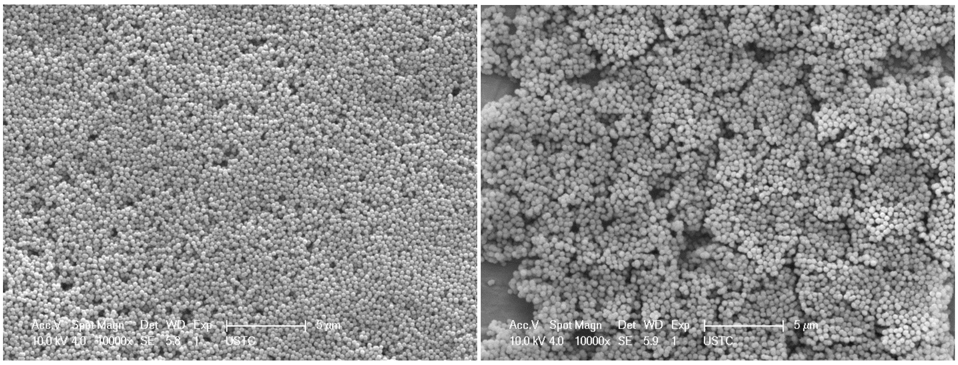


**Fig. S1** Low magnification SEM images of the 260 nm $Fe_3O_4$ hollow spheres (left) and 360 nm dual-shelled $Fe_3O_4$@PDA hollow spheres prepared under the DA concentration of 4.4 mM (right).

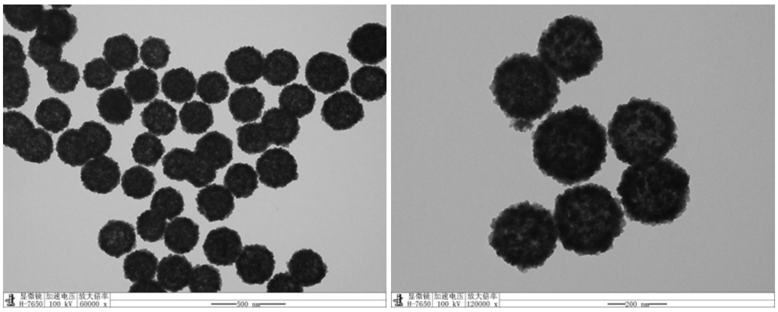


**Fig. S2** TEM images of the pristine $Fe_3O_4$ hollow spheres with average size of 260 nm.

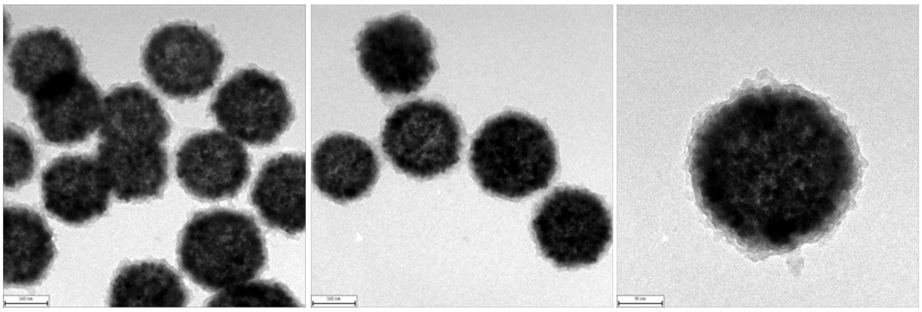


**Fig. S3** TEM images of the single dual-shelled $Fe_3O_4$@PDA hollow spheres with different shell thickness 20 nm.

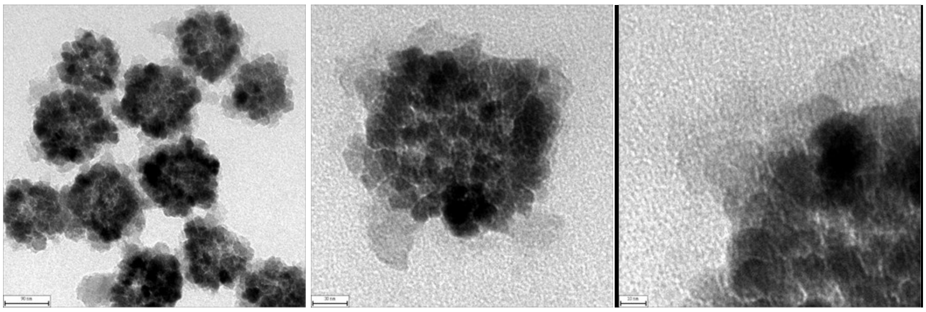


**Fig. S4** TEM images of the dual-shelled $Fe_3O_4$@PDA hollow spheres (based on 120 nm nanospheres, DA concentration: 0.4 mM ) with different magnification.

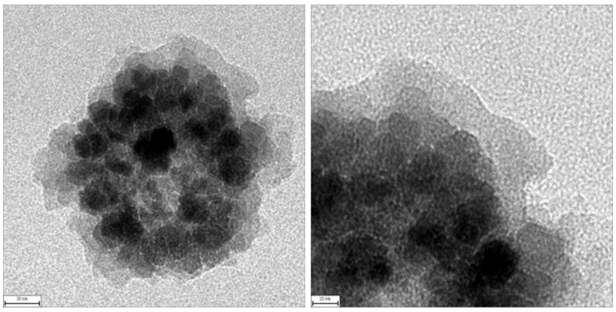


**Fig. S5** TEM images of the dual-shelled $Fe_3O_4$@PDA hollow nanospheres (based on 120 nm nanospheres, DA concentration: 0.7 mM ) with different magnification.

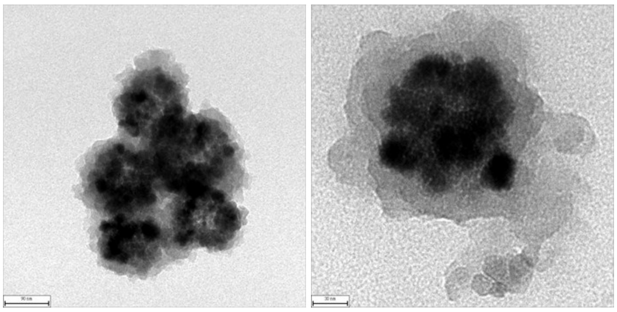


**Fig. S6** TEM images of the dual-shelled $Fe_3O_4$@PDA hollow nanospheres (based on 120 nm microspheres, DA concentration: 1 mM) under the 4 h reaction.

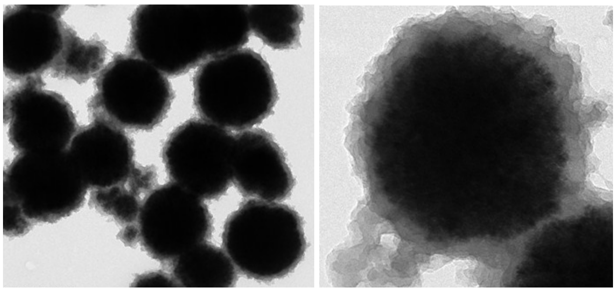
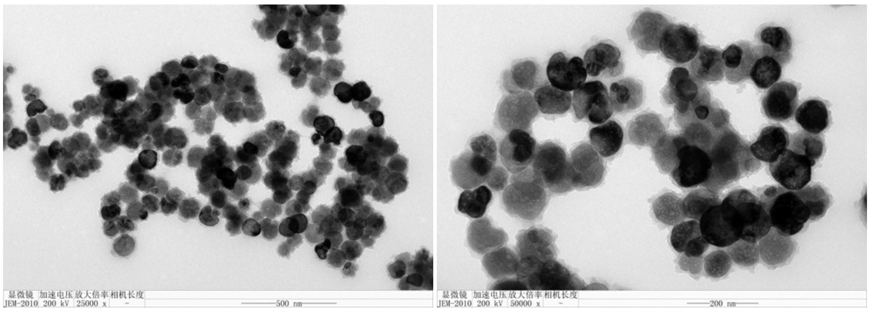


**Fig. S7** TEM images of the $Fe_3O_4$@PDA core/shell spheres (based on 300 nm microspheres) with different magnification.



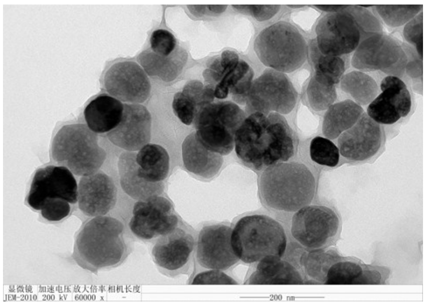


**Fig. S8** TEM images of the $Fe_3O_4$@PDA core/shell spheres (based on 100 nm porous nanospheres) with different magnification.

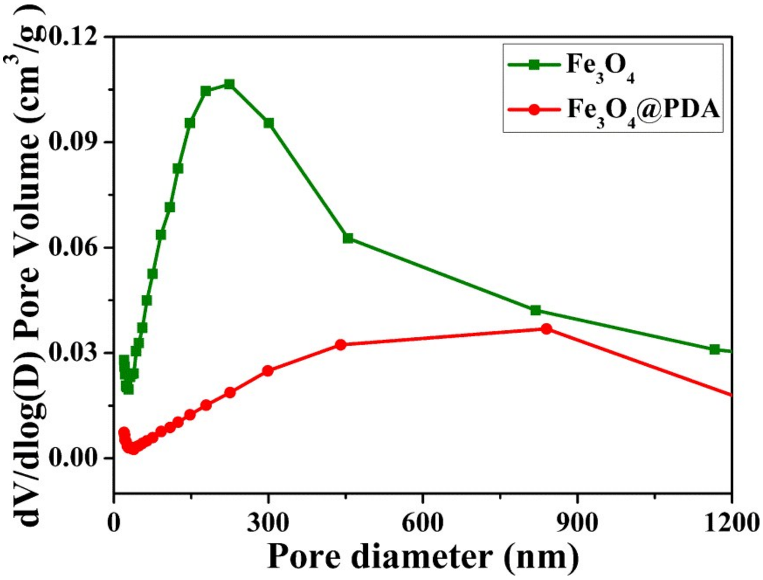


**Fig. S9** Barrett–Joyner–Halenda (BJH) pore size distribution plot of 260 nm hollow $Fe_3O_4$ microspheres and 300 nm $Fe_3O_4$@PDA particles with shell thickness of 20 nm.

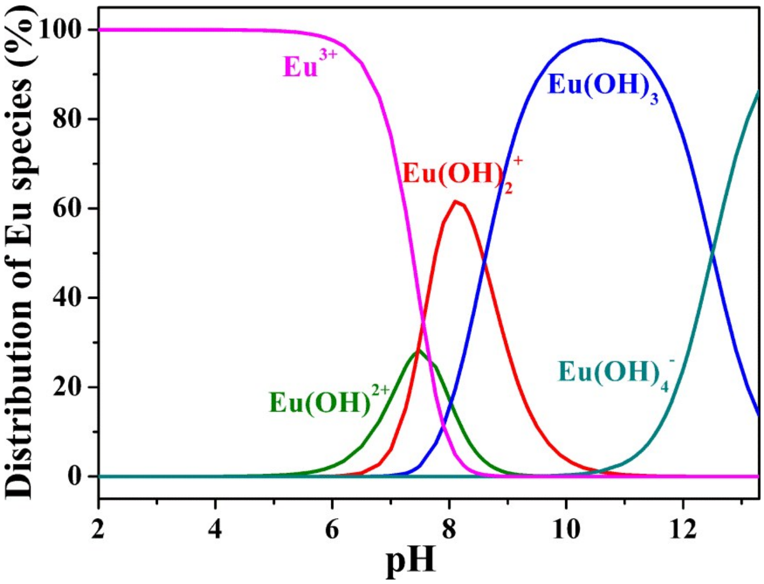


**Fig. S10** Distribution of Eu(III) species as a function of solution pH values.