

Supporting Information for

Novel Polyazamacrocyclic Receptor Decorated Core-shell Superparamagnetic Microspheres for Selective Binding and Magnetic Enrichment of Palladium: Synthesis, Adsorptive Behavior and Coordination Mechanism

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Experimental

Sample preparation for XPS survey and FT-IR Spectrophotometry

30 mg $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{DOTA}$ microspheres were dispersed in 1.0 mol/L HNO_3 solution containing 1.0 g/L Pd(II) in a 25 °C constant temperature oscillator. After shaking for 24 h to reach the equilibrium, the resulting $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{DOTA-Pd}$ microspheres were separated and rinsed with water and ethanol, respectively, followed by drying at 45 °C under vacuum for 12 h.

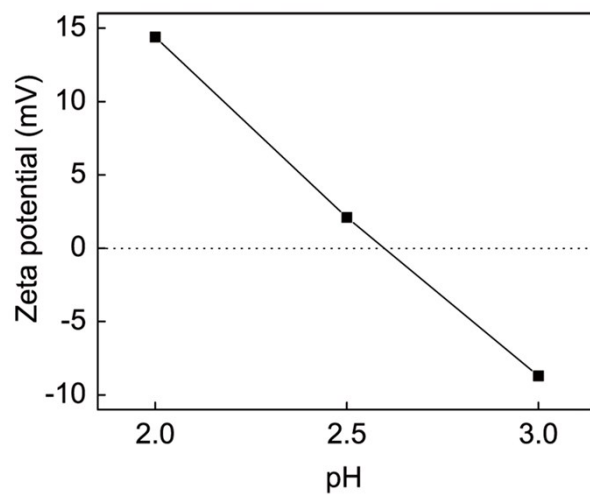


Figure S1. Zeta-potential curve of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{DOTA}$ as a function of pH

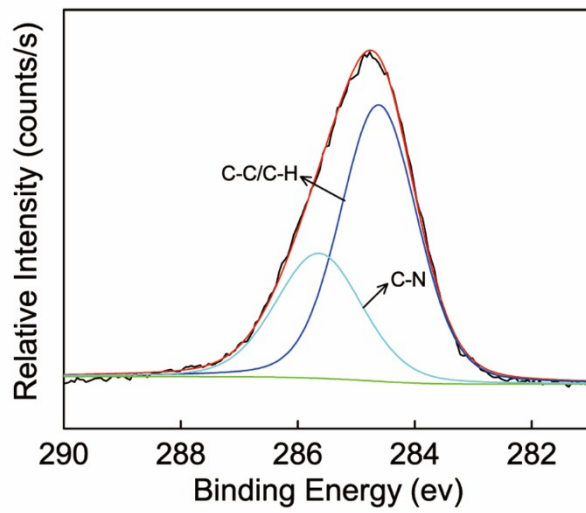


Figure S2. C 1s high resolution spectra of APTES-modified Fe₃O₄@SiO₂

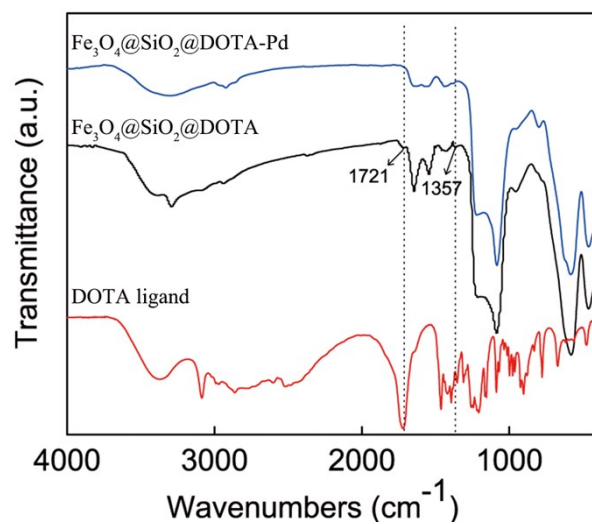


Figure S3. FT-IR spectra of DOTA ligand, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{DOTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{DOTA-Pd}$

Table S1 Pore structure parameters and specific surface area of Fe₃O₄@SiO₂ microspheres

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
Fe ₃ O ₄ @SiO ₂	34.8	0.039	2.5

Table S2. Comparison of Pd(II) adsorption ability of Fe₃O₄@SiO₂@DOTA with other sorbents

Sorbents	Experimental conditions	q_{\max} ($\mu\text{mol/g}$)	Ref.
Gallic acid resin	T=293 K, 0.01 mol/L HNO ₃	81.9	1
Anthracite LKAU-4	T=298 K, pH=1.5 HCl	9.3	2
Sulfur-impregnated CMK-3/S	T=298 K, 1.0 mol/L HCl	900.0	3
Crown ether decorated silica particles	T=298 K, 1.0 mol/L HNO ₃	771.3	4
Calixcrown ether decorated silica particles	T=298 K, 1.0 mol/L HNO ₃	1510.1	5
Fe ₃ O ₄ @SiO ₂ @DOTA	T=298 K, 1.0 mol/L HNO ₃	105.3	This work

Table S3. Elution of Pd(II) loaded on the Fe₃O₄@SiO₂@DOTA by different eluents

Eluents	Recovery rate of Pd (II) (%) ^{a,b}
H ₂ O	0.5 ± 0.3
Acetic acid	1.2 ± 0.6
0.1 mol/L HCl	2.3 ± 0.5
Oxalic acid	4.6 ± 0.3
1 mol/L HNO ₃	5.1 ± 0.6
3 mol/L HNO ₃	6.4 ± 0.8
5% thiourea	83.2 ± 0.6
1% thiourea + 0.5 mol/L HNO ₃	93.2 ± 0.9

^a Adsorption condition: [Pd]= 50 mg/L, [HNO₃]= 1.0 mol/L, m/v=0.01 g/mL, contact time=15 h, T=298 K

^b Elution condition: m/v= 0.01 g/mL, contact time=15 h, T=298 K

Table S4. Composition of APTES-modified Fe₃O₄@SiO₂, Fe₃O₄@SiO₂@DOTA, and Fe₃O₄@SiO₂@DOTA-Pd by XPS

Samples	XPS analysis (<i>wt. %</i>)			
	C	N	O	Pd
APTES-modified Fe ₃ O ₄ @SiO ₂	35.39	9.05	55.36	Null
Fe ₃ O ₄ @SiO ₂ @DOTA	41.15	14.04	44.81	Null
Fe ₃ O ₄ @SiO ₂ @DOTA-Pd	43.15	12.38	43.09	1.38

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