

Electronic Supporting Information for

Novel Core-shell Structured Superparamagnetic Microspheres Decorated with Macrocylic Host Molecules for Specific Recognition and Magnetic Removal of Pb(II)

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Contents

Experimental Section

1. Chemicals	S-2
2. Modification of 1,3-CalixCrown host molecule	S-2
3. Characterization	S-2
4. The reuse of Fe ₃ O ₄ @SiO ₂ @1,3-Calixcrown	S-2

Supporting Scheme

Scheme. S1 Synthetic route of 1,3-CalixCrown host molecule	S-4
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Supporting Figures

Figure. S1 TGA spectra of the magnetic microspheres	S-5
Figure. S2 Size distribution of Fe ₃ O ₄ microspheres	S-6
Figure. S3 TEM image of Fe ₃ O ₄ microspheres	S-7
Figure. S4 Magnetic separation process by the use of Fe ₃ O ₄ @SiO ₂ @1,3-Calixcrown	S-8
Figure. S5 Removal efficiency of Pb(II) in low concentration solutions	S-9
Figure. S6 Adsorption capacity of Pb(II) and isotherm fitted by Freundlich model	S-10

Supporting Table

Table. S1 Elemental analysis of the magnetic microspheres	S-11
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Experimental Section

1. Chemicals. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), anhydrous sodium acetate, ethylene glycol (EG), tetraethyl orthosilicate (TEOS), 3-chloropropyltriethoxysilane (CPTES) and di-*n*-butyltindilaurate (DBTL) were purchased from Sigma-Aldrich. Deionized water was obtained from a Milli-Q water purification system. All other chemicals of analytical grade, including metal nitrates $\text{M}(\text{NO}_3)_2 \cdot m\text{H}_2\text{O}$ ($\text{M}=\text{Pb}$, Cu, Ni, Cd, Ba, Zn, Sr), nitric acid, ammonium hydroxide and other reagents, were commercially obtained and used without further purification.

2. Modification of 1,3-CalixCrown host molecule. 1,3-di(2-propoxy)calix[4]-arene-crown-6 (2.133 g, 3 mmol) was dissolved in 100 mL acetic anhydride and maintained under $-15\text{ }^\circ\text{C}$. Under stirring, a mixture of 50 mL acetic anhydride, 50 mL acetic acid and 0.64 g fuming nitric acid was added dropwise to the above solution. After 3 h reaction, the reaction mixture was warmed slowly to room temperature and stirred overnight. Then, the mixture was poured into ice water under vigorous agitation to obtain light yellow colored product. The crude product was purified to result in **[0]** by recrystallization in methanol/ether ($v/v = 5:2$) solution (Yield: 93%).

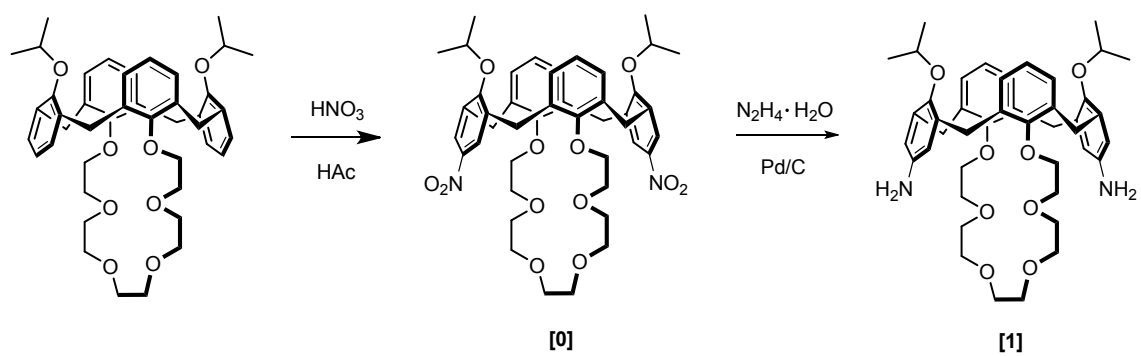
0.8 g **[0]** (1 mmol) and 0.05 g Pd/C catalyst were dispersed in 80 mL ethanol, followed by the addition of 10 mL hydrazine hydrate. The reduction reaction was carried out under reflux for 3 h under stirring. Then, the residual of the catalyst was separated by filtration. After evaporating the solvent in the filtrate, white product **[1]** was obtained, which was then purified by recrystallization in ethyl acetate (Yield: 87%).

3. Characterization. Power X-ray diffraction (XRD) patterns of the products were obtained on a diffractometer with Cu K α radiation, with a scan step of 2° and a scan range between 10° and 80° . Fourier transform infrared (FTIR) spectra were obtained in KBr a pellet in the range $4000\text{-}400\text{ cm}^{-1}$ on Nicolet Nexus 470. The morphology of the microspheres was investigated by LEO 1530 scanning electron microscope (SEM), coupled with energy-dispersive X-ray spectroscopy (EDX) for determination of sample composition. Transmission electron microscopy (TEM) images were recorded by use of H-7650 transmission electron microscopes with an accelerating voltage of 200 KV. Magnetic properties (M-H curves) were measured at 300 K by cycling the external field between -10 and 10 KOe 730T Vibrating Sample Magnetometer (VSM). The concentration of the metal ions was determined by ICP-AES (SPECTRO ARCOS SOP).

4. The reuse of $\text{Fe}_3\text{O}_4@\text{SiO}_2@1,3\text{-Calixcrown}$. To evaluate the reusability of 1,3-Calixcrown modified magnetic silica microspheres, the lead ion adsorbed by $\text{Fe}_3\text{O}_4@\text{SiO}_2@1,3\text{-Calixcrown}$ were eluted with 0.1 mol/L HNO_3 solution, and the concentration of eluted lead were analysed by ICP-AES. It was found that 64% Pb (II) were released from magnetic composite. After elution, the $\text{Fe}_3\text{O}_4@\text{SiO}_2@1,3\text{-CalixCrown}$ microspheres were washed by

deionized water, followed by drying at 100°C for 6 h. The regenerated materials were used for the removal of Pb(II) under the same condition, the remove efficiency of Fe₃O₄@SiO₂@1,3-Calixcrown towards Pb(II) was still more than 80%.

Supporting Scheme



Scheme S1. Synthetic route of 1,3-CalixCrown host molecule

Supporting Figures

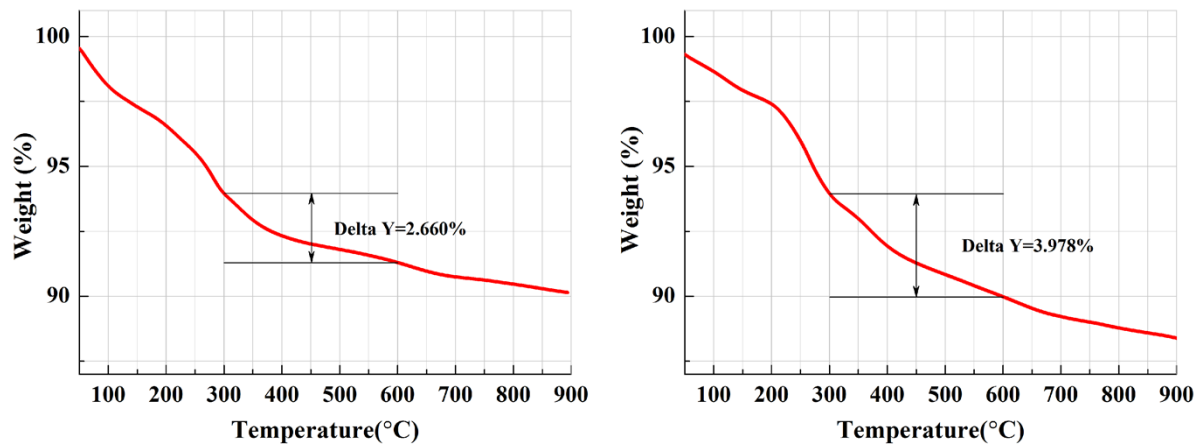


Figure S1. TGA spectra of Fe₃O₄@SiO₂ (a) and Fe₃O₄@SiO₂@1,3-CalixCrown (b) microspheres.

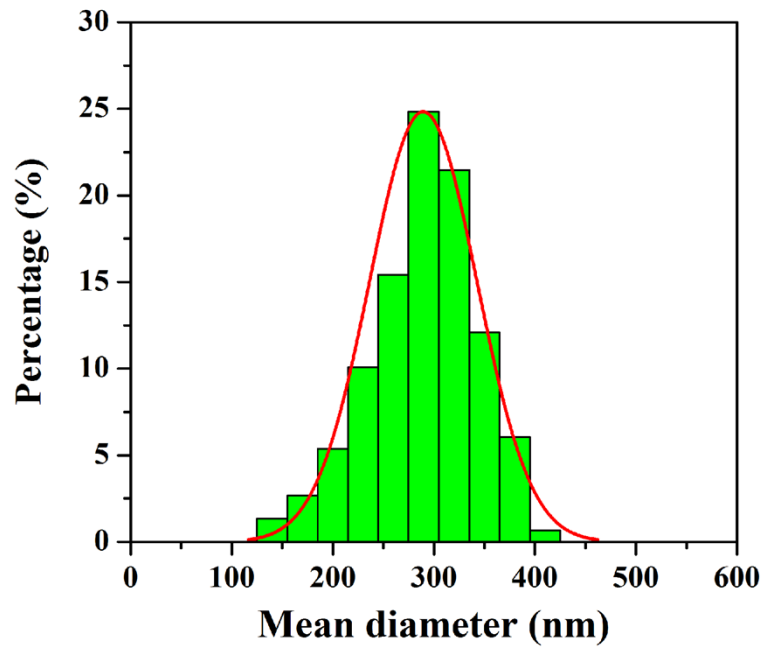


Figure S2. Size distribution of Fe₃O₄ microspheres

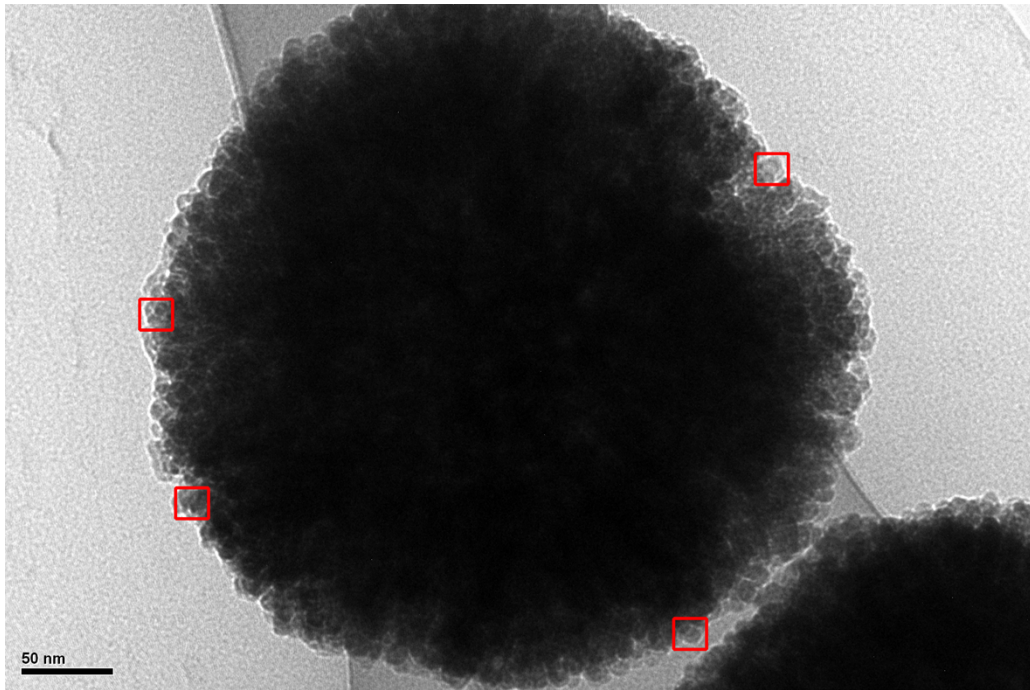


Figure S3. TEM image of Fe₃O₄ microspheres

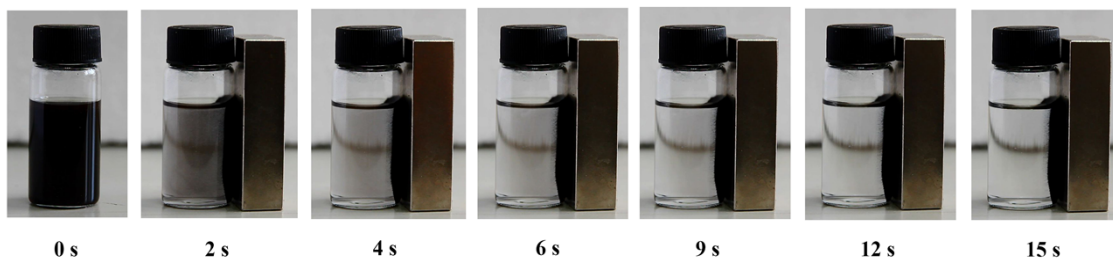


Figure S4. Film screenshots of magnetic separation process by the use of $\text{Fe}_3\text{O}_4@\text{SiO}_2@1,3\text{-Calixcrown}$

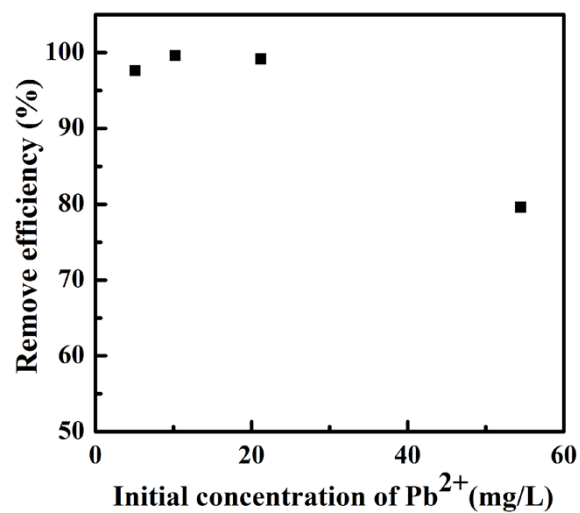


Figure S5. Removal efficiency of Pb(II) in low concentration solutions. The initial Pb(II) concentrations were 5.1 mg/L, 10.2 mg/L, 21.1 mg/L and 54.5 mg/L. It can be seen that the Fe₃O₄@SiO₂@1,3-CalixCrown has a high removal efficiency for the Pb(II) in low concentration.

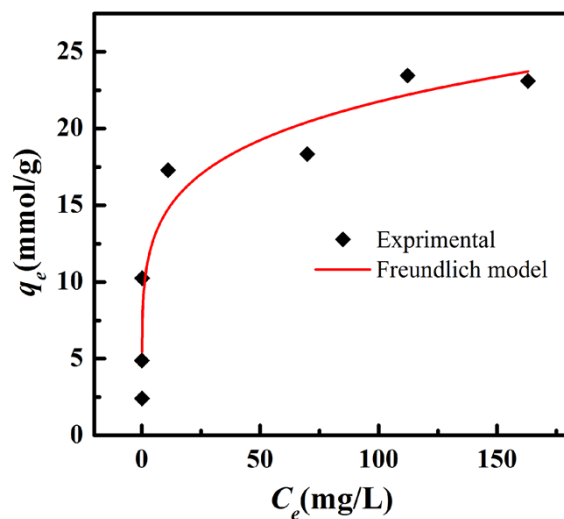


Figure S6. Adsorption capacity of Pb(II) and isotherm fitted by Freundlich model. The experiment was performed in Pb(II) solutions with initial concentration varying from 5~200 mg/L. It can be roughly estimated that the adsorption capacity in equilibrium is about 24 mmol/g.

Supporting Table

Table S1. Elemental analysis of the magnetic microspheres

Samples	Elemental analysis		
	wt% C	wt% H	wt% N
Magnetic precursor	4.06	0.58	0.19
Fe ₃ O ₄ @SiO ₂ @1,3-CalixCrown	4.98	0.46	0.21