Table of contents entry

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

Rong Yi, Gang Ye[*], Dengfang Pan, Fengcheng Wu, Mingfen Wen, and Jing Chen[*]
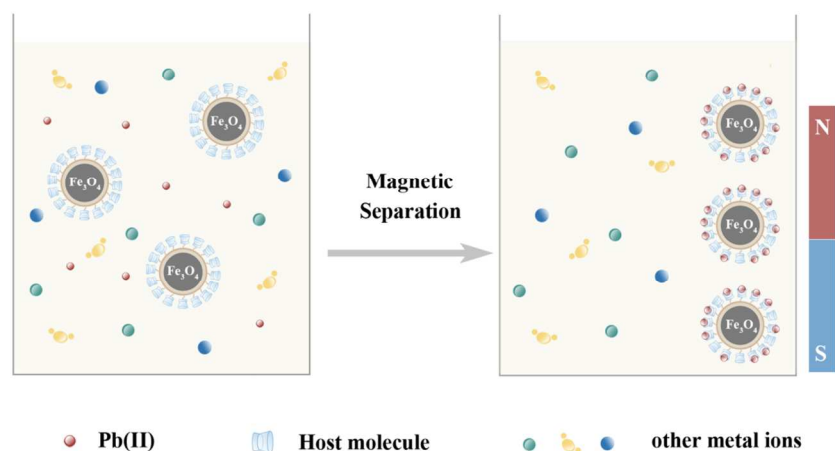
Specific recognition and highly-efficient magnetic separation of Pb(II) by a new class of core-shell structured superparamagnetic microspheres bearing calixcrown host molecules with size-fitted cavities.

Journal of Materials Chemistry A

PAPER

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

Rong Yi,[a] Gang Ye,[*a] Dengfang Pan,[a] Fengcheng Wu,[a] Mingfen Wen,[a] and Jing

Chen[*a]

In this work, core-shell structured superparamagnetic microspheres with highly specific recognition ability towards Pb(II) based upon host-guest interactions was developed for the first time. The four-component microsphere consists of a superparamagnetic Fe_3O_4 core, two-layer silica serving as protection shell and functional spacer, and a macrocyclic host molecule 1,3-alternate calix[4]arene-crown-6 decorated periphery. The magnetic microspheres showed easy dispersibility, high magnetization (45.8 emu/g) and sensitive response to the applied magnetic field. Reversible magnetic separation could be accomplished within 15 seconds. The superparamagnetic property guaranteed the magnetic microspheres a convenient redispersion. Batch experiments revealed that the magnetic microspheres had remarkable selectivity to Pb(II) in the presence of various interfering metals. Besides, the magnetic microspheres showed good stability against acid erosion for 20 days. The characterization of structure, micro-morphology and magnetic properties of the microspheres were detailed. The recognition mechanism concerning the host-guest interaction and the effect of neighbor amino donors was discussed. This work offered a facile and efficient pathway to build host molecule functionalized core-shell magnetic microspheres, which has great potential for molecular recognition and separation applications.

Introduction

Magnetic nanoparticles (MNPs) have recently aroused considerable interest due to their key role in advanced magnetic separation system, which is of great significance in various fields like biotechnology/biomedicine, environmental remediation, etc.[1-6] According to the principle of finite-size effect, each magnetic nanoparticle can become a single domain when the particle size is below a critical value, and exhibits superparamagnetic behaviors.[7-9] Such superparamagnetic nanoparticle has large constant magnetic moment and shows fast response to applied magnetic fields with negligible remanence and coercivity. However, an inevitable problem associated with the particles in nano size is the strong tendency to form agglomerates to minimize the surface energy.[10,11] In addition, the naked magnetic particles are chemically unstable when exposed directly to the environment, especially in harsh conditions. Hence, successful application of the magnetic nanoparticles is highly dependent on the improvement of stability.

The most prevailing strategy to stabilize the magnetic nanoparticles is to develop an impenetrable protective layer, which results in the core-shell structured nano- or micro-particles.[12] Among the miscellaneous protection methods, coating the magnetic nanoparticles with a silica shell has been widely recognized for its advantages such as stability under aqueous conditions, and easy control of interparticle interactions through varying the shell thickness.[13-15] Moreover, a well-developed silica shell provides extensive possibility for further surface functionalization, which diversifies the magnetic nanoparticles to meet the specific requirement of practical applications.[16-19]

Recent years have witnessed the progress of host-guest chemistry from the basis of molecular recognition to the construction of novel functional materials. Lately, host-guest chemistry has been connected with magnetic nano-materials which opened new perspectives for the development of magnetic assisted separation system with unique recognition ability.[20-22] Leung's group reported a novel pathway to purify amine monofunctional gold nanoparticles (1-AuNPs) in a hydrogen-bonded supramolecular manner by using crown-ether-decorated superparamagnetic iron oxide nanoparticles.[23] Besides, Böhmer et al. covalently attached *tetra*-CMPO-calix[4]arenes to magnetic silica particles for the magnetically

assisted separation of lanthanides and actinides from acidic solutions.[24] However, up to now, reports on successful preparation of host molecule functionalized magnetic nanoparticles, especially those with superparamagnetic behavior, are very rare in literature. More efforts should be directed to this promising area before it can be relied on for environmental and biomedical separation applications.

Lead ion is a highly-concerned heavy metal pollutant which will bring substantial harm to the central nervous system and digestive system of human body after the long-term accumulation.[25,26] In this study, a novel kind of core-shell structured superparamagnetic microsphere decorated with 1,3-alternate calix[4]arene-crown-6 host molecules at the periphery was developed for selective recognition and magnetic separation of Pb(II). To the best of our knowledge, this is the first example of superparamagnetic material with superior selectivity towards Pb(II) based upon host-guest interaction. The host molecule functionalized superparamagnetic microspheres, labeled as $Fe_3O_4@SiO_2@1,3$-CalixCrown, showed high magnetization, very fast response in applied magnetic field, and long-term stability against acid erosion. Structure, morphology and magnetic properties of the superparamagnetic microspheres were fully characterized. Selective removal of Pb(II) against various divalent interfering metal ions was accomplished. The binding mechanism regarding the role of the calixcrown host molecules was discussed.

Experimental section

Synthesis and modification of host molecule. A macrocyclic calixcrown host molecule **[1]** bearing amino donor groups was designed to functionalize the magnetic particles. To obtain the host molecule, 1,3-alternate calix[4]arene-crown-6 (1,3-CalixCrown) was first synthesized and purified based on the improvement of the method reported by Ungaro et al.[27] Then, amino donor groups, also as reactive sites for the 1,3-CalixCrown molecules to be anchored to the magnetic particles, were site-selectively introduced at the 1,3-alternate benzene rings. The decoration process was involved with a two-step reaction, namely, selective nitration followed by catalytic amination, which is described in the [†]ESI (Scheme S1). The structure of all the intermediates and final products were confirmed by ^{1}H NMR,^{13}C NMR and FT-IR spectra.[28]

Synthesis of $Fe_3O_4@SiO_2$. Magnetic Fe_3O_4 core was prepared through a solvothermal reaction.[17] Briefly, 2.70 g of $FeCl_3·6H_2O$ and 7.2 g of sodium acetate were dissolved in 100 mL ethylene glyol under magnetic stirring. A homogeneous yellow solution was obtained and transferred into a Teflon-lined stainless-steel autoclave with capacity of 200 mL. The autoclave was sealed and heated at 200 °C for 8 h, and cooled to room temperature. The black magnetite particles were gathered with the help of magnet and washed several times with ethanol and deionized water. The products were dried in vacuum at 60 °C for 12 h.
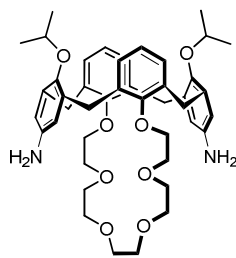
[1]

Then, the magnetite core was coated with a thin silica layer through a sol-gel approach, forming $Fe_3O_4@SiO_2$ microspheres with

core-shell structure. Typically, the magnetic Fe_3O_4 particles (0.5 g) were treated with 0.1 mol/L HCl aqueous solution by ultrasonication for 20 min. Then, the magnetite particles were washed with deionized water and dispersed in a mixture of ethanol (200 mL), deionized water (50 mL) and concentrated ammonia aqueous solution (2.5 mL, 28 wt.%), followed by the injection of tetraethyl orthosilicate (TEOS, 0.5 mL). After stirring at room temperature for 6 h, the $Fe_3O_4@SiO_2$ microspheres were separated by use of a magnet, washed with ethanol and deionized water, and then dried in vacuum at 60 °C for 6 h.
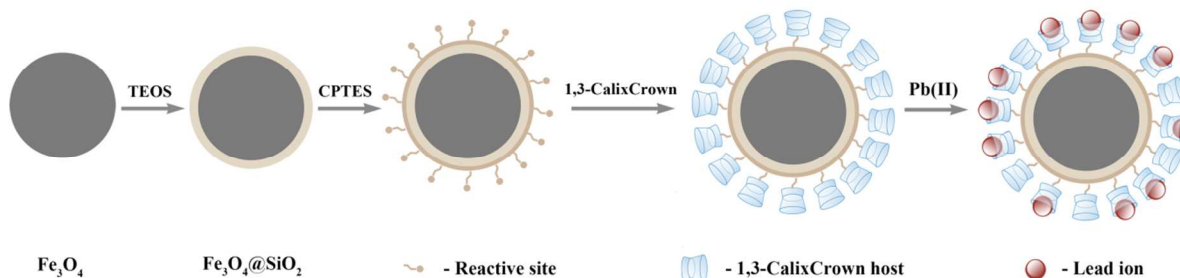
Synthesis of $Fe_3O_4@SiO_2@1,3$-CalixCrown. 0.5 g $Fe_3O_4@SiO_2$ microspheres were suspended in 100 mL dry toluene by ultrasonic treatment for 15 min, followed by addition of 50 mL dry toluene containing 0.5 mL of 3-chloropropyltriethoxysilane (CPTES). Under nitrogen atmosphere, the mixture was heated at 115 °C for 48 h reflux with mechanical agitation. Then, the CPTES-functionalized $Fe_3O_4@SiO_2$ microspheres were collected by a magnet and washed with toluene, ethanol, and diethyl ether, respectively. The particles were dried under vacuum at 60 °C for 12 h.

1.0 g CPTES-functionalized $Fe_3O_4@SiO_2$ microspheres and 0.5 g **[1]** were mixed in 200 mL THF and dispersed *via* ultrasound for 15 min. 1.3 g K_2CO_3 and 0.9 g KI were added to promote the reaction. Under N_2 protection, the reaction was allowed to take place at 80 °C for 48 h. Then, the product was separated and washed alternatively with ethanol and deionized water until the washing liquor was neutral and no potassium cation was detected by atomic absorption spectroscopy (AAS). Finally, the product was dried at 60 °C vacuum oven for 24 h.

Recognition behavior and magnetic separation. The recognition and separation ability of the $Fe_3O_4@SiO_2@1,3$-CalixCrown microspheres towards metals was investigated by batch operation in 10 mL plastic tube immersed in 25 °C constant temperature bath oscillator. Metal solutions containing Pb(II) as well as other six kinds of interfering divalent cations (Ba(II), Cd(II),Cu(II), Ni(II), Zn(II) and Sr(II)) were prepared with the initial concentration of each metal is 50 mg/L. 40 mg $Fe_3O_4@SiO_2@1,3$-CalixCrown was added into 2 mL metal solution. After vigorous agitating in swing bed at 25 °C for 2 h, functionalized magnetic particles were separated by using an NdFeB magnet. The concentration of the residual metal ions in the aqueous phase was measure by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The removal rate of the metal ions was calculated based on material balance.

Results and discussions

Synthesis of $Fe_3O_4@SiO_2@1,3$-CalixCrown. The synthesis procedure of the core-shell structured superparamagnetic microspheres decorated with calixcrown host was illustrated in Scheme 1. First, uniform magnetite microspheres were obtained via a solvothermal synthesis, which afforded a good control of the shape and size distribution of the particles.[1] The magnetic core was then coated with a thin layer of silica as protective shell by the typical Stöber method.[29] Weighing the enhancement of stability and the sacrifice of the magnetism of the Fe_3O_4 core, the coating thickness was deliberately tuned by controlling the concentration of ammonia and the ratio of TEOS to H_2O. The coated silica layer was readily for further modification by CPTES to result in a second silica layer which could offer lots of reactive sites for the attachment of the host molecules 1,3-CalixCrown. Meanwhile, the modification of the 1,3-CalixCrown by introducing NH_2 substitutes with appropriate orientation was also a prerequisite. In this work, NH_2 substitutes were introduced at the *para*-position of the 1,3-alternate benzene rings with isopropyl groups. It has been reported that the coordination effect of the amino donors and cyclic ether groups will

2 | *J. Mater. Chem.A.*, 2014, **00**, 1-3

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Scheme 1.Illustration of the synthetic procedure of $Fe_3O_4@SiO_2@$1,3-CalixCrown and the recognition to Pb(II).

bring benefits for metal recognition.[30] Finally, the NH_2 substituted 1,3-CalixCrown was grafted to the CPTES modified $Fe_3O_4@SiO_2$ microspheres through a nucleophilic reaction, which was promoted by the addition of excess potassium carbonate and potassium iodide.

Structure and morphology characterization. The magnetic core of the $Fe_3O_4@SiO_2@$1,3-CalixCrown was characterized *via* powder X-Ray diffraction (XRD), while the silica coating and the anchored host molecules were identified by FT-IR spectra. Figure 1 shows the XRD patterns of the as-synthesized Fe_3O_4 microspheres (b) and the coated product $Fe_3O_4@SiO_2$ (c). Since the position and strength of the diffraction peaks are completely in coincidence with that of the standard pattern of magnetite (JCPDS card 19-629) (a), it can be concluded that the obtained Fe_3O_4 microspheres have a face center cubic (fcc) phase. The coating of the silica shell *via* the sol-gel method did not affect the phase structure of the magnetic core.
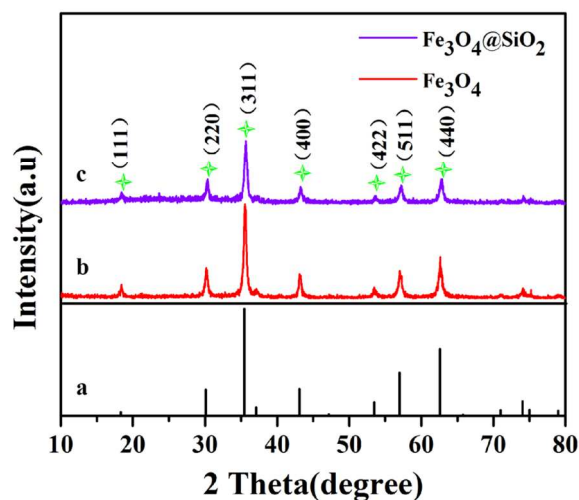
core-shell structured magnetic microspheres. In addition, based on the C, H, N elemental analysis of the product and the precursor ([†]ESI, Table S1), it was calculated that the amount of the 1,3-CalixCrown anchored to the surface of the magnetic microspheres was about 1.28 *wt*.%. This result was in agreement with that obtained by the weight loss estimation based on the TGA curves in the temperature range of 300-600 ^oC ([†]ESI, Figure S1).[28]
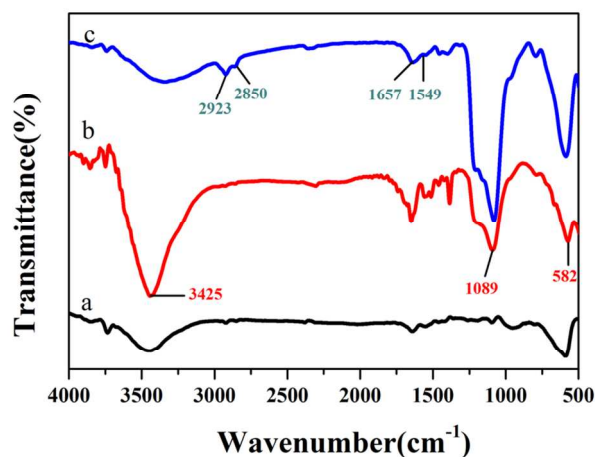

Figure 2. FT-IR spectra of (a) Fe_3O_4 particles; (b) $Fe_3O_4@SiO_2$ microspheres; (c) $Fe_3O_4@SiO_2@$1,3-CalixCrown.

Figure 1. X-ray diffraction (XRD) patterns of (a) standard magnetite, (b) Fe_3O_4 particles and (c) $Fe_3O_4@SiO_2$ microspheres.

The FT-IR spectra of the Fe_3O_4 microspheres (a), $Fe_3O_4@SiO_2$ (b) and $Fe_3O_4@SiO_2@$1,3-CalixCrown (c) were displayed in Figure 2. After the coating reaction, $Fe_3O_4@SiO_2$ showed evident resonances at 3425 cm^{-1} and 1089 cm^{-1}, which were derived from the stretching vibration of Si-OH and Si-O bonds. For the $Fe_3O_4@SiO_2@$1,3-CalixCrown product, the grafting of the host molecules resulted in the appearance of signals at around [1610 cm^{-1}, 1549 cm^{-1}] and [2923 cm^{-1}, 2850 cm^{-1}], contributed by the benzene rings and the methylene groups in the 1,3-CalixCrown molecules. The NH- group showed resonances at 3330 cm^{-1} and 1657 cm^{-1}, respectively. The signal of C-O stretching vibration in the cyclic ether was partially overlapped by the broad Si-O peaks. These results confirmed the successful attachment of the host molecule 1,3-CalixCrown to the

The micro-structure and morphology of the magnetite particles and the core-shell structured products were studied. Visual evidences obtained by SEM and TEM analysis were given in Figure 3. It can be seen from the SEM image (a) that the solvothermal synthetic method in our study resulted in the Fe_3O_4 microspheres with good spherical shape and uniform size. The TEM image (b) shows that the Fe_3O_4 microspheres have an average diameter of about 300 nm, which is also in accordance with the measurement by laser particle analyzer ([†]ESI, Figure S2). Moreover, it can be observed that every microsphere was composed of a large number of magnetite nanoparticles (~ 15 nm) ([†]ESI, Figure S3). This is essential to afford the microspheres with superparamagnetic property. Because, based upon the finite-size effects mentioned above, magnetic nanoparticles exhibit superparamagnetic behavior only if their size is below a critical value, which is determined by the balance between the magnetostatic energy (ΔE_{MS}) and domain-wall energy (E_{dw}).[8,9] The critical size of the magnetic nanoparticles is dependent on the material but is typically around 10-20 nm.[1] The TEM image of $Fe_3O_4@SiO_2$ (c) shows that well-developed silica coating with the thickness about 20 nm was formed after the sol-gel process.

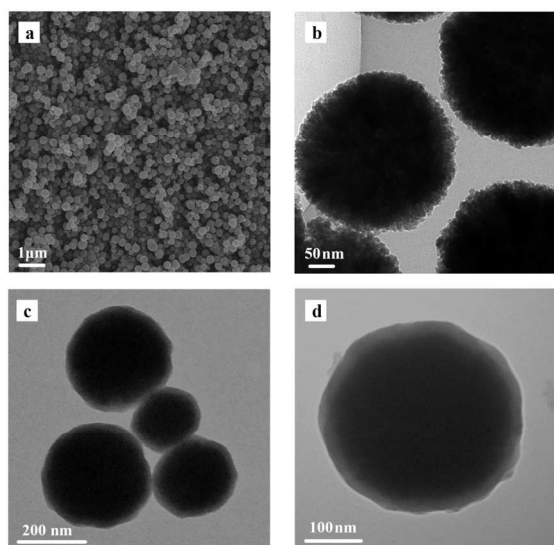Figure 3. SEM and TEM images of Fe_3O_4 (a, b), $Fe_3O_4@SiO_2$ microspheres (c) and $Fe_3O_4@SiO_2@1,3$-CalixCrown (d).

Further modification by CPTES and the grafting of host molecules did not compromise the structure of the coated microspheres due to the robustness of the silica protective layer. Fig. 2(d) shows that the final 1,3-CalixCrown functionalized magnetic material reserves the spherical shape and core-shell structure.

Magnetic properties and stability. The magnetic property of the Fe_3O_4 core and the 1,3-CalixCrown functionalized microspheres was investigated by a vibrating magnetometer. The magnetic hysteresis loops (Figure 4(a)) obtained at 300 K showed that the saturation magnetization values of the as-synthesized Fe_3O_4 core, $Fe_3O_4@SiO_2$, CPTES modified $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2@1,3$-CalixCrown microspheres were 80.4, 61.0, 58.3 and 45.8 emu/g, respectively. After coating with two silica layers and anchoring with host molecules, the $Fe_3O_4@SiO_2@1,3$-CalixCrown microspheres still maintained high magnetization saturation. Meanwhile, superparamagnetic phenomena were confirmed for all the samples due to the absence of remanence after the applied magnetic field was removed and negligible coercivity, which can be observed in the

hysteresis loops near the zero point. This is due to the existence of a great amount of magnetic Fe_3O_4 nanoparticles smaller than the critical size in the microspheres.

The dispersion and magnetic separation of the host molecule functionalized microspheres was examined and recorded by digital camera (Figure 4(b)). Because of the superparamagnetic property and the screening effect of the silica layer, the $Fe_3O_4@SiO_2@1,3$-CalixCrown microspheres could be readily and stably dispersed in water. Then, very fast separation of the magnetic microspheres was observed under the applied external magnetic field (NdFeB magnet, 2000 Oe). Only lasting 15 seconds, all the magnetic microspheres were aggregated to the wall of the vial next to the magnet ([†]ESI, film screenshots in Figure S4). This excellent magnetic responsibility should be attributed to the high magnetization saturation of the $Fe_3O_4@SiO_2@1,3$-CalixCrown microspheres. Once the magnet was moved away, redispersion of the magnetic microspheres occurred quickly with a slight shaking. The excellent dispersibility and the magnetic sensitivity of the $Fe_3O_4@SiO_2@1,3$-CalixCrown microspheres are important advantages for practical use of magnetic separation.

The stability of the core-shell structured microspheres against acid erosion was also evaluated, as compared with the naked magnetite microspheres. The samples were soaked in 1.0 mol/L nitric acid solution. The amount of the leached ferric ions was measured by spectrophotometer. Figure 5 gives the variation of the leached Fe^{3+} in the solution during a 20-day treatment. It can be seen that the $Fe_3O_4@SiO_2$ microspheres have satisfactory stability in the strong acidic environment. The nitric acid caused no obvious damage to the silica coatings. On the contrary, the naked Fe_3O_4 particles, due to the lack of silica protective layer, show a fast degradation. These results reaffirm the necessity of the core-shell protection strategy for the improvement of magnetic microsphere materials. For $Fe_3O_4@SiO_2@1,3$-Calixcrown, the grafting of the host molecules did not compromise the protective coating. The intact silica layer could be distinctly seen in the TEM image (Figure 3(d)). So the Fe_3O_4 core in the final product can be well-reserved in acidic solutions. Meanwhile, the crown ether molecules anchored to solid substrate materials have been proved with good resistance against hydrolysis in strong acid media in our previous work.[31,32] Therefore, it is believed that $Fe_3O_4@SiO_2@1,3$-CalixCrown microspheres should be stable enough for practical applications.
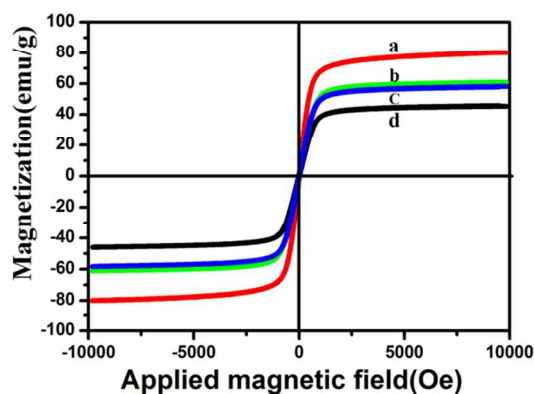
(A)
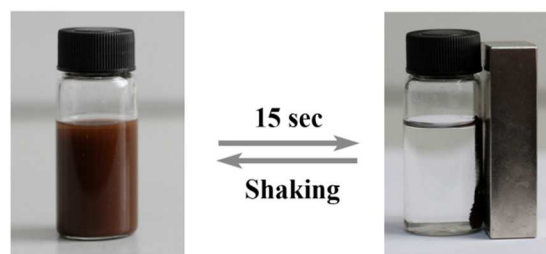
(B)

Figure 4. (A) The magnetic hysteresis loops of the magnetic microspheres. (a) Fe_3O_4 core, (b) $Fe_3O_4@SiO_2$, (c) CPTES modified $Fe_3O_4@SiO_2$, (d) $Fe_3O_4@SiO_2@1,3$-CalixCrown; (B) the magnetic separation-redispersion process of $Fe_3O_4@SiO_2@1,3$-CalixCrown.

4 | *J. Mater. Chem.A.*, 2014, **00**, 1-3

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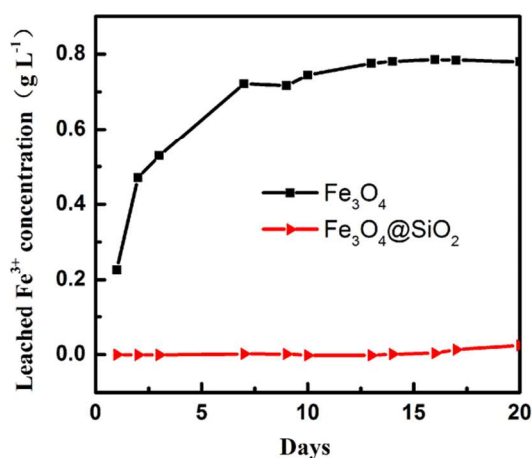
Figure 5. Stability study of the magnetite microsphere and the core-shell structured $Fe_3O_4@SiO_2$.

Recognition towards Pb(II) and mechanism discussion. The recognition behavior towards metal cations was investigated *via* batch adsorption. A multicomponent solution containing Pb(II) and other 9 kinds of interfering species including alkali/alkaline-earth metal ions and typical divalent metals was prepared with the initial concentration of 50 mg/L for each metal. The host molecule functionalized magnetic microspheres were mixed with the solution, followed by shaking for 2 h. After that, the $Fe_3O_4@SiO_2@1,3$-CalixCrown microspheres were separated by a magnet, and the residue metal cations were measured by ICP-AES. Blank experiment was also carried out by the use of the CPTES modified $Fe_3O_4@SiO_2$. Figure 6 summarized the removal rate of the metals. For a better comparison, the removal rate of Pb(II) (about 77%) was normalized to be 1. Obviously, $Fe_3O_4@SiO_2@1,3$-CalixCrown showed highly selective recognition to Pb(II) in the presence of the above-mentioned several interferences. Since the blank material contributed only a little, the remarkable selectivity of the $Fe_3O_4@SiO_2@1,3$-CalixCrown should be reasonably attributed to the host molecule 1,3-CalixCrown. To our knowledge, this is the first example of superparamagnetic particles with specific recognition towards Pb(II) based on host-guest interaction. Generally, calixcrown molecules have been known as good ligands of alkali and alkaline-earth metal ions. However, the $Fe_3O_4@SiO_2@1,3$-CalixCrown showed no affinity towards Na(I), K(I), Mg(II), etc. This might be explained by the conformational change and/or orientation constraint of the 1,3-CalixCrown molecules after covalently anchoring to the $Fe_3O_4@SiO_2$ microspheres.

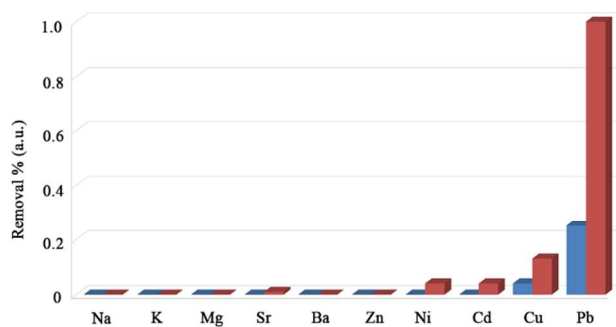Figure 6. Selective removal of Pb(II) by the $Fe_3O_4@SiO_2@$ 1,3-CalixCrown microspheres (right columns) and the precursor (left columns) in a multicomponent system.[Metal]=50 mg/L, phase ratio=0.02 g/mL, pH=5.5, contact time=2 h.
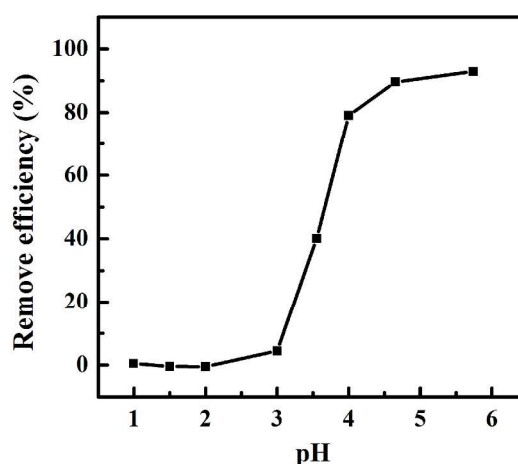

Figure 7. Effect of pH on the remove efficiency of Pb(II) by $Fe_3O_4@SiO_2@1,3$-Calix Crown.

Batch experiments in Pb(II) solutions with very low concentration also showed that the microspheres had a high removal efficiency for trace Pb(II) (†ESI, Figure S5). The fitting of the equilibrium data suggested that the adsorption isotherm of $Fe_3O_4@SiO_2@1,3$-CalixCrown towards Pb(II) might be in agreement with Freundlich model (†ESI, Figure S6). Besides, the lead ions binded by the host molecules can be effectively eluted by using 0.1 mol/L HNO_3. About 64% captured Pb(II) was released in every operation. After three-time elution, the $Fe_3O_4@SiO_2@1,3$-CalixCrown microspheres were washed by deionized water, followed by drying at 100°C for 6 h. The recycled microspheres still maintain more than 80% of the adsorption efficiency towards Pb(II).

The detailed mechanism regarding the interaction between the calixcrown host and the lead ion has not been completely recognized at this moment. As we know, a calixcrown molecule has both a soft π-donor cavity composed of benzene rings and a hard oxygen cavity at the crown ether unit. Eighteen-membered crown ethers such as dicyclohexyl-18-crown-6 and its derivatives have been reported to show great affinity and selectivity to Pb(II).[33] In our case, it is believed that the cyclic ether unit in the calixcrown host should be responsible for the specific recognition to Pb(II). Meanwhile, we carried out the experiment to investigate the effect of H^+ in the solutions. The result revealed that the binding ability of the $Fe_3O_4@SiO_2@1,3$-CalixCrown microspheres was sensitive to the change of pH in the range of 3 to 4 (Figure 7). This does not conform to the rule for Pb(II) separation materials built based upon dicyclohexyl-18-crown-6 host molecules,[33,34] but is similar to the phenomena of those containing nitrogen ligands.[35-37] As we mentioned above, the calixcrown host molecule was decorated with amino substituents in the benzene rings at 1,3- alternate position of the π-donor cavity. In the 1,3-alternate conformation, the benzene groups can be also involved with the metal-binding behavior by forming the metal-π interaction, because of their adjacency to the cyclic ether ring.[27] The amino donors should then play an role for the recognition behavior of the $Fe_3O_4@SiO_2@1,3$-CalixCrown microspheres by influencing the electron distribution of the benzene rings at 1,3-alternate positions. In brief, the coordination effect by the cyclic ether rings and the amino-substituted benzene groups might better explain the recognition behavior to Pb(II). However, in-depth investigation like theoretical calculation and molecular modeling needs to be done for a more specific explanation.

Conclusions

In summary, we reported the synthesis of a new class of core-shell structured superparamagnetic microspheres bearing host molecules 1,3-CalixCrown for selective and magnetic separation of Pb(II). The magnetic microspheres exhibited easy dispersibility and excellent stability in the aqueous media due to the superparamagnetic property and the existence of the silica protective shell. The high magnetization (45.8 emu/g) and sensitivity to the applied magnetic field afforded a very fast magnetic separation. Specific recognition towards Pb(II) was realized based on the host-guest interaction between the 1,3-CalixCrown host and the lead ions. The mechanism concerning the binding reaction was discussed. This work provides a facile and efficient approach for the development of host molecule functionalized superparamagnetic microspheres, which have great potential for molecular recognition and sensing applications.

Acknowledgements

Notes and references

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†Electronic Supplementary Information (ESI) available. Chemicals, synthesis details, characterization, elemental analysis (C, H, N), and TGA curves of the magnetic microspheres, and file screenshots of the magnetic separation process. See DOI: 10.1039/b000000x/

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6 | *J. Mater. Chem.A.*, 2014, **00**, 1-3

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