

Preparation of Fe₃O₄@SiO₂@PLL Core-Shell Nanoparticles for Potential Application for Heavy Metal Ion Removal

Yi-han Ma, Qing-han Zhou *

Abstract— The Fe₃O₄@SiO₂@PLL core-shell nanoparticles were prepared by functionalization of magnetic Fe₃O₄ nanoparticles with 3-aminopropyl trimethoxane (APTMS) and Poly(L-lysine) (PLL) as a novel sorbent for heavy metal ion removal in water. The Fe₃O₄@SiO₂@PLL nanoparticles were prepared by a three-step process: (i) surface modification of Fe₃O₄ nanoparticles by APTMS to form Fe₃O₄@SiO₂, (ii) surface functionalization of Fe₃O₄@SiO₂ nanoparticles by ring opening polymerization to form a Fe₃O₄@SiO₂@PZLL nanoparticles, and (iii) deprotection of PZLL to form the Fe₃O₄@SiO₂@PLL nanoparticles. The chemical structure of the Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂@PZLL, and Fe₃O₄@SiO₂@PLL was characterized by FTIR and XRD. The nano-size, zeta-potential, and surface morphologies of the core-shell nanoparticles were analyzed by DLS and SEM. The core-shell nanoparticles will be further studied on their removal efficiency for heavy metal ions such as Cr^{VI} from the aqueous medium, and the effects of different factors such as initial adsorbent concentration, adsorption time, adsorption dosage, pH, and temperature in the adsorption experiment will be furtherly studied.

Index Terms— Poly(L-lysine), adsorbent, magnetic nanoparticles, removal of heavy metal ions.

I. INTRODUCTION

It is still challenging to provide adequate clean water for the world's growing population, which is one of the major challenges mankind faces. In last decades, enormous amounts of contaminated aqueous effluents have been generated by industrial activities. Among the contaminated aqueous effluents, heavy metals are the most common pollutants that harm the aqueous environment and damage health of human, animals and plants, because they are non-biodegradable and may cause metabolic and physiological problems. Therefore, international organizations such as the World Health Organization (WHO) and Centre for Disease Control (CDC) regulate heavy metal ions as hazardous substances. Thus, many approaches have been utilized to remove heavy metal ions, including chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation, and flocculation.

Among these methods for removal of heavy metal ions, adsorption is considered as a promising technique owing to

its high removal efficiency, low cost, ease of operation, and reusability. Therefore, adsorption method has been extensively used in various water purification processes. Some efficient adsorbents have been employed in heavy metal ion adsorption, such as carbon, zeolite clay, graphene, carbon nanotubes, bio-adsorbents, and various metal oxides. However, a more efficient waste water treatment system with novel adsorbents that can be removed quickly and recycled is necessary.

Magnetic separation is a low-cost and efficient method of separating magnetic materials from aqueous systems through the application of an external magnetic field. Although there have been many significant developments in the application of magnetic nanoparticles, maintaining the stability of these particles for a long time without agglomeration or precipitation is still a challenge. Moreover, bare magnetite nanoparticles are rather susceptible to air oxidation, which hindered the further development in wastewater treatment. Recently, polymeric chelating materials are widely used in the removal of metal ions due to their high adsorption capacities and selectivity. Thus, the nanosorbent with chelating polymer coatings and inorganic magnetic inner core, have attracted much more attention for water treatment due to the facile collection under a magnetic field without contamination.

In this study, Fe₃O₄@SiO₂@PLL was prepared by a three-step process. The magnetic nanosorbent and related nanoparticles were characterized by FT-IR, DLS, and SEM. Finally, based on the experimental results the as prepared Fe₃O₄@SiO₂@PLL core-shell nanoparticles were considered as a promising magnetic nanosorbents for potential use in removal of heavy metal ions from water.

II. EXPERIMENTAL

Materials

Ferric trichloride (FeCl₃ · 6H₂O) and Ferrous chloride (FeCl₂ · 4H₂O) were purchased from Chengdu xindu MuLan town industrial development zone, Hydrobromic acid in glacial acetic acid (HBr/AcOH, 33% w/v), 3-aminopropyl trimethoxane (APTMS), trifluoroacetic acid (TFA) were purchased from Beijing J&K Chemical, ammonium persulfate, citric acid, ammonium hydroxide, nitric acid, hexyl hydride, ethyl alcohol, ethyl acetate and solvents were purchased from Chengdu Kelon chemical reagent company. PZLL-NCA was synthesized by our group.

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Synthesis of Fe₃O₄ nanoparticles

FeCl₃·6H₂O 2.70 g and FeCl₂·4H₂O 1.00 g were added into a three-necked flask, and then 60.00 mL of deionized water was added under nitrogen atmosphere, and mechanically stirred (700 r/min) at 80 °C. After 30 min stirring, 20.00 mL ammonia was added to adjust the pH to 9~10, and underwent another 30 min stirring under N₂ protection. Finally, 2.00 mL citric acid was added, the reaction was carried out at 90 °C for 90 min. When cooled to room temperature, the upper layer liquid was removed, and washed with ethanol and deionized water for several times. The obtained Fe₃O₄ colloid was placed into a vacuum oven, and dried for 3 h to obtain Fe₃O₄ magnetic nanoparticles.

Preparation of Fe₃O₄@SiO₂ magnetic nanoparticles

0.13 g Fe₃O₄ magnetic nanoparticles were added to a three-necked flask containing 15.00 mL of ethanol and 15.00 mL of deionized water. The mixed solution was ultrasonically dispersed for 10 min, and then mechanically stirred (250 r/min) for 30 min at 80°C. 1.00 mL of APTMS were added into the three-necked flask. And the reaction was carried out at room temperature for 3.5 h under N₂. Then, the supernatant was removed by centrifugation, and washed with deionized water for several times. The obtained colloid was placed in a vacuum oven at 50 °C for 24 h to obtain the Fe₃O₄@SiO₂ magnetic nanoparticles.

Preparation of Fe₃O₄@SiO₂@PZLL magnetic nanoparticles

0.10 g Fe₃O₄@SiO₂ magnetic nanoparticles were added into 10.00 mL of DMF and ultrasonically dispersed for 10 min. PZLL-NCA (2.00 g, 4.00 mmol) was added into three-necked flask at room temperature with gently stirring for 36 h. Finally, the solvent was removed, and the product solution was precipitated in diethyl ether. The raw product was then washed with distilled water and ethanol for several times, and was dried by vacuum to obtain the Fe₃O₄@SiO₂@PZLL magnetic nanoparticles.

Preparation of Fe₃O₄@SiO₂@PLL

Fe₃O₄@SiO₂@PLL (0.70 g, 0.07 mmol) was added into 25.00 mL of NaOH solution. The reaction was carried out for 12 h under N₂ at room temperature. Then the solvent was removed under reduced pressure, the obtained solid was further dispersed in distilled water, and then washed with diethyl ether for several times. Then the raw product was dried by vacuum to obtain a white powder.

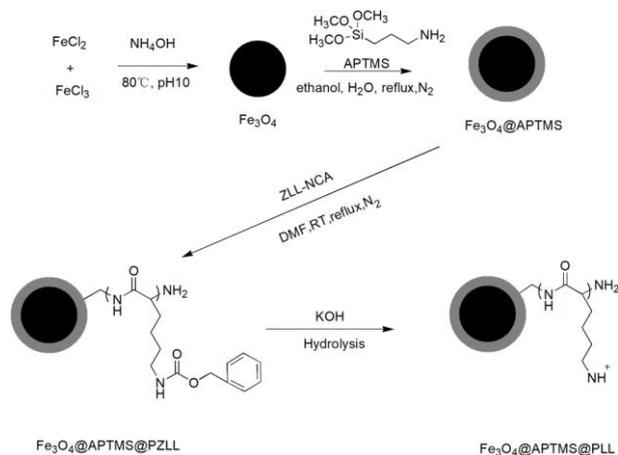


Fig. 1 Synthetic scheme for the preparation of Fe₃O₄@SiO₂@PLL.

III. RESULTS AND DISCUSSION

Preparation and characterization of the Fe₃O₄@SiO₂@PLL magnetic nanoparticles

The Fe₃O₄ nanoparticles were prepared by co-precipitation method. Then APTMS was used to decorate the surface of the Fe₃O₄ nanoparticles to obtain a -NH₂ modified magnetic nanoparticles. By the ring opening polymerization, the PZLL-NCA was used to synthesize the Fe₃O₄@SiO₂@PZLL magnetic nanoparticles. Finally, the Fe₃O₄@SiO₂@PLL was prepared via deprotection of the PZLL by a hydrolysis reaction. Each step of the preparation process was characterized by FT-IR.

The FT-IR spectra of Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂@PZLL, and Fe₃O₄@SiO₂@PLL were shown in the Fig.2. As shown in Fig.2, the peak around 580 cm⁻¹ could be ascribed to the stretching vibration of Fe-O. In the FT-IR spectrum of Fe₃O₄@SiO₂, it was indicated that the absorption peak at 1020 cm⁻¹ could be ascribed to the stretching vibration of Si-O. For the FT-IR spectrum of Fe₃O₄@SiO₂@PZLL, the absorption peak around 1128, 1651, and 1700 cm⁻¹ corresponded to the C-O-C group, C=O group in the amide bond, and C=O group in the ester bond. The peak at 3290 cm⁻¹ can be ascribed to the N-H stretching vibration. For the FTIR spectrum of Fe₃O₄@SiO₂@PLL. The peak at 1020 cm⁻¹ corresponded to Si-O. The peak at 1637 cm⁻¹ and 3430 cm⁻¹ could be ascribed to C=O and N-H group. Based on the FTIR spectra, it was suggested that the nanoparticles of Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂@PZLL, and Fe₃O₄@SiO₂@PLL were successfully prepared.

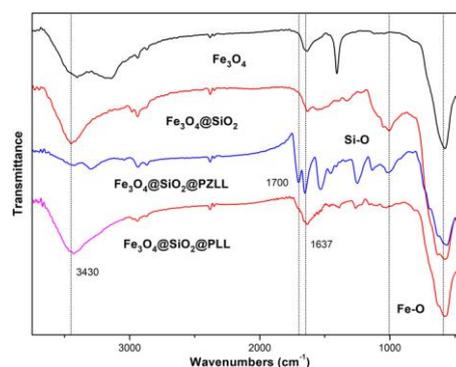


Fig. 2 FT-IR spectra of Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂@PZLL, and Fe₃O₄@SiO₂@PLL.

The diffractogram for nanoparticles of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$ were shown in Fig. 3, and all of the diffraction peaks were consistent with the database in JCPDS file. The presence of sharp and intense peaks confirmed the formation of highly crystalline Fe_3O_4 . Besides the crystalline Fe_3O_4 diffraction peaks, the XRD pattern of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$ exhibits the clear reflections of Fe_3O_4 phase with low intensity compared with Fe_3O_4 nanoparticles. The XRD results suggested the successful preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$, and the lower crystallinity of the Fe_3O_4 particles in $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$ samples can be explained by the polymer modification on the surface of Fe_3O_4 nanoparticles.

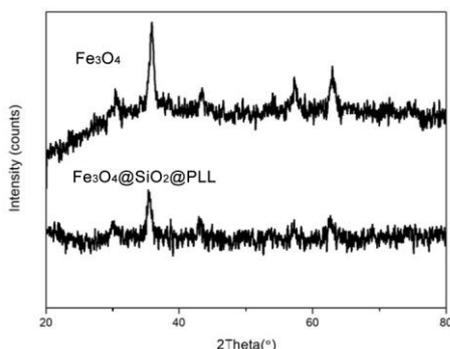


Fig. 3 XRD patterns of the Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$.

The zeta potential was further investigated to characterize the surface property of each samples. The zeta potential of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$ was 24 mV, 32 mV, and 1.46 mV, which indicated the positively charged $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$ nanoparticles were successfully prepared.

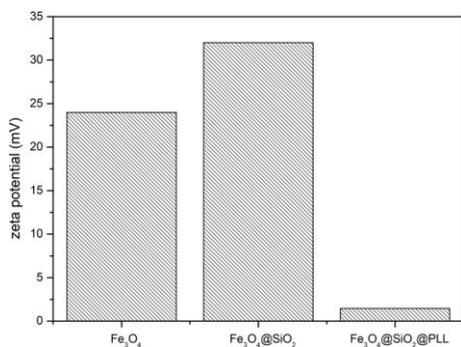


Fig. 4 Zeta potential of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$.

As shown in the Fig. 5, the size change of the nanoparticles was investigated by DLS. Fig. 5 revealed that Fe_3O_4 nanoparticles exhibited a constant average size of 110 nm, and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles showed an average size of 120 nm after the modification by APTMS, which proved that SiO_2 was successfully coated onto the surface of Fe_3O_4 magnetic nanoparticles. Finally, the $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$ nanoparticles were of ~190 nm. It was indicated that the $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$ nanoparticles were successfully prepared by with PLL coating.

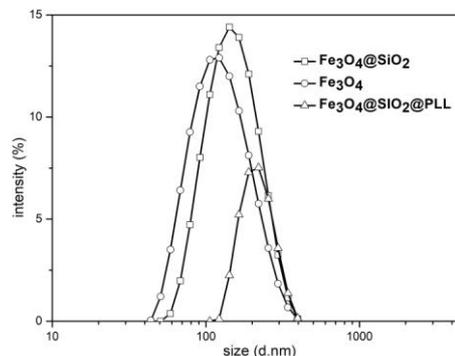


Fig. 5 Zeta potential of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$.

The SEM photos of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$ were shown in Fig.6. The size of Fe_3O_4 magnetic nanoparticles is about 80 nm. The size of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$ nanoparticles were about 160nm, which proved that SiO_2 and PLL was successfully coated onto the surface of Fe_3O_4 magnetic nanoparticles. The SEM results were consistent with the DLS measurement indicating the successfully modification of the Fe_3O_4 magnetic nanoparticles.

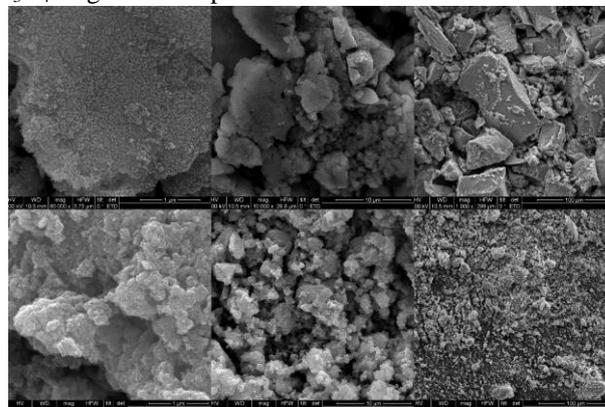


Fig. 6 SEM photos of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$ nanoparticles.

IV. CONCLUSION

In this experiment, the novel magnetic nanosorbent, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$, was prepared by a three-step process. The chemical structures and morphology of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$ were fully characterized by FT-IR, DLS, and SEM. Based on the experimental results, the as prepared magnetic nano-adsorbent can be used as a promising reusable nano-materials for potential use in heavy metal ion removal.

V. ACKNOWLEDGMENT

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REFERENCES

- [1] R. Hasanzadeh, P.-N. Moghadam, N. Bahri-Laleh and M. Sillanpää. "Effective removal of toxic metal ions from aqueous solutions: 2-Bifunctional magnetic nanocomposite base on novel reactive PGMA-MAn copolymer@ Fe_3O_4 nanoparticles". Journal of colloid and interface science, vol. 490, 2017, pp. 727-746.
- [2] S. Jin, B.-C. Park, W.-S. Ham, L. Pan and Y.-K. Kim. Effect of the magnetic core size of amino-functionalized Fe_3O_4 -mesoporous SiO_2 core-shell nanoparticles on the removal of heavy metal ions[J].Colloids

- and Surfaces A: Physicochemical and Engineering Aspects, Vol. 531, 2017, pp. 133-140.
- [3] X. Xin, Q. Wei, J. Yang, L. Yan, R. Feng, G. Chen, B. Du and H. Li. Highly efficient removal of heavy metal ions by amine-functionalized mesoporous Fe₃O₄ nanoparticles. *Chemical Engineering Journal*, Vol. 184, 2012, pp. 132-140.
- [4] J. Wang, S. Zheng, Y. Shao, J. Liu, Z. Xu and D. Zhu. Amino-functionalized Fe₃O₄@ SiO₂ core-shell magnetic nanomaterial as a novel adsorbent for aqueous heavy metals removal. *Journal of Colloid and Interface Science*, Vol. 349(1), 2010, pp. 293-299.
- [5] S. Jin, B.-C. Park, W.-S. Ham, L. Pan and Y.-K. Kim. Effect of the magnetic core size of amino-functionalized Fe₃O₄-mesoporous SiO₂ core-shell nanoparticles on the removal of heavy metal ions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 531, 2017, pp. 133-140.
- [6] J.-L. Weidman, R.-A. Mulvenna and B.-W. Boudouris, W.-A. Phillip. Nanoporous block polymer thin films functionalized with bio-inspired ligands for the efficient capture of heavy metal ions from water. *ACS applied materials & interfaces*, Vol.9(22), 2017, pp. 19152-19160.
- [7] R. Sahraei and M. Ghaemy. Synthesis of modified gum tragacanth/graphene oxide composite hydrogel for heavy metal ions removal and preparation of silver nanocomposite for antibacterial activity. *Carbohydrate polymers*, Vol. 157, 2017, pp. 823-833.
- [8] P. Miao, Y. Tang and L. Wang. DNA modified Fe₃O₄@Au magnetic nanoparticles as selective probes for simultaneous detection of heavy metal ions. *ACS applied materials & interfaces*, Vol.9(4), 2017, pp. 3940-3947.
- [9] T. Wen, Q. Fan, X. Tan, Y. Chen, C. Chen, A. Xu and X. Wang. A core-shell structure of polyaniline coated protonic titanate nanobelt composites for both Cr (VI) and humic acid removal. *Polymer Chemistry*, Vol. 7(4), 2016, pp. 785-794.
- [10] S. Wang, K. Wang, C. Dai, H. Shi and J. Li. Adsorption of Pb²⁺ on amino-functionalized core-shell magnetic mesoporous SBA-15 silica composite. *Chemical Engineering Journal*, Vol. 262, 2015, pp. 897-903.
- [11] C. Ren, X. Ding, H. Fu, W. Li, H. Wu and H. Yang. Core-shell superparamagnetic monodisperse nanospheres based on amino-functionalized CoFe₂O₄@ SiO₂ for removal of heavy metals from aqueous solutions. *RSC Advances*, Vol. 7, 2017, pp. 6911-6921.
- [12] B. Samiey, C.-H. Cheng and J. Wu. Organic-inorganic hybrid polymers as adsorbents for removal of heavy metal ions from solutions: A review[J]. *Materials*, Vol. 7(2), 2014, pp. 673-726.
- [13] H.-N.-M.-E. Mahmud, A.-K.-O. Huq and R.-B. Yahya. The removal of heavy metal ions from wastewater/aqueous solution using polypyrrole-based adsorbents: a review. *RSC Advances*, Vol. 6(18), 2016, pp. 14778-14791.