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ORIGINAL PAPER

Preparation of superparamagnetic *β*-cyclodextrin-functionalized composite nanoparticles with core–shell structures

Ruixue Li · Shumei Liu · Jianqing Zhao ·
Hideyuki Otsuka · Atsushi Takahara

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Abstract In this article, we report an original and feasible protocol for the preparation of superparamagnetic *β*-cyclodextrin-functionalized composite nanoparticles with core–shell structures via cross linking reaction on the surface of carboxymethyl *β*-cyclodextrin-modified magnetite (Fe_3O_4) nanoparticles by using epichlorohydrin as a crosslinking agent. The structure and morphology of the prepared composite nanoparticles were studied by Fourier transform infrared spectrometry, X-ray diffraction measurement, transmission electron microscopy and the thermogravimetric analysis. The results show that the prepared roughly spherical composite nanoparticles (diameter about 10–20 nm) with core–shell structures turned out to be magnetite nanoparticles surface-surrounded by a layer of cross-linked CM-*β*-cyclodextrin polymer. Results of vibrating sample magnetometry testing and inclusive behaviour studying confirmed the superparamagnetism with saturation magnetization value of 52.0 emu/g in an external applied magnetic field of 20000 Oe and inclusion functionality of the composite nanoparticles consisting of magnetite cores and *β*-cyclodextrin moiety, which implies very important applications in targeting drug delivery technology and separation for specific substances.

Keywords *β*-Cyclodextrin · Magnetite (Fe_3O_4) nanoparticles · Composite nanoparticles

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R. Li · S. Liu (✉) · J. Zhao
College of Materials Science and Engineering, South China University of Technology, 381 Wushan Road, Guangzhou, 510640, China
e-mail: shumeiliuchn@gmail.com

H. Otsuka · A. Takahara
Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

Introduction

In recent years, β-cyclodextrin (β-CD) plays important roles in many disciplines such as supramolecular chemistry, analytical chemistry, biomedicine and catalysis [1–3]. β-CD is a torus-shaped cyclic oligosaccharide consisting of seven α-1,4-linked D-glucose units arranged in a circle with a hydrophilic exterior surface and a hydrophobic interior cavity. The special structure affords it remarkable ability to form inclusion complexes with many organic compounds and biological molecules [4–6]. Because of this unique supramolecular behaviour, β-CD and its derivatives including β-cyclodextrin polymers (β-CDP) have been extensively researched in the fields of drug delivery system, separating and absorption of material, environmental protection devices and functional catalysts, etc. [7–11].

Nano-sized materials offer many important advantages due to their unique size as well as physical properties and have become one of the most important research and development frontiers in modern science. Nowadays, magnetite (Fe_3O_4) nanoparticles, for their good biocompatibility, superior superparamagnetic property, non-toxicity and easy preparation process, are becoming a focus of relative research areas [12–15]. They have attracted increasing attention and enormous interest in biomedical applications including enzyme encapsulation, DNA transfection, biosensors, bioseparators and targeting drug delivery system [16–20]. Most of the above mentioned applications require the magnetite nanoparticles to keep chemical stability, uniformity in size, and fine dispersion status in liquid media [21]. Magnetite nanoparticles with superparamagnetism can be easily magnetized with an external magnetic field and demagnetized immediately once the external magnetic field is removed, not retaining any magnetism. However, due to high specific surface energy and anisotropic dipolar attraction, magnetite nanoparticles tend to aggregate together into larger clusters which lead to a possible loss of superparamagnetism and limit their applications. Also, it is well known that magnetite (Fe_3O_4) has a high magnetic saturation value compare to maghemite (γ-Fe_2O_3), and if exposed to oxygen environment, magnetite (Fe_3O_4) can change its oxidation status and transform to maghemite (γ-Fe_2O_3) gradually which may result in serious degradation of magnetic performance and still limit their applications [22, 23].

In this study, surface modification is a frequently used method to keep superior magnetic properties of magnetite nanoparticles. One way is to capsulate magnetite nanoparticles with a layer of polymeric materials so that both the aggregation of magnetite nanoparticles due to the high specific surface energy and the transformation of magnetite (Fe_3O_4) to maghemite (γ-Fe_2O_3) attributed to the reaction of Fe(II) cations with contacted oxygen molecules can be effectively prevented. Furthermore, the capsulated polymer layer with functional groups can always afford magnetite nanoparticles some new superior properties [24–26]. Recently, researchers reported several successful designings and preparation methods of cyclodextrin-functionalized superparamagnetic nanoparticles or their spherical aggregates by conjugating cyclodextrin (CD) units onto the surface of magnetite nanoparticles [27–30]. On one hand, the innermost magnetite nanoparticles can sense and respond to an externally applied magnetic field. On the other hand, the outermost cyclodextrin moiety can function as inclusion sites and specific containers for drugs and biomolecules. Generally, the preparation strategies can be divided into two steps. First, magnetite nanoparticles are surface decorated by modifiers with active amino groups (–NH_2). Then, the previously synthesized cyclodextrin derivatives with some active groups such as tosylate groups (–OTs) or carboxyl (–COOH) are covalently bonded with amino groups (–NH_2) and thus grafted onto the surface of magnetite nanoparticles. Usually, the synthesis of used CD derivatives and the surface modification of magnetite nanoparticles with amino groups (–NH_2) are complicated and the oxidation of magnetite nanoparticles can not be prevented so effectively. In this article, we propose a convenient and feasible protocol for the preparation of superparamagnetic β-CD-functionalized composite nanoparticles with core–shell structures via cross-linking reaction on the surface of carboxymethyl β-CD (CM-β-CD)-modified magnetite nanoparticles by using epichlorohydrin (EP) as a cross-linking agent. As shown in Fig. 1, CM-β-CD with carboxyl groups which can coordinate with the surfaces of metal oxide nanoparticles is utilized to surface-modify magnetite (Fe_3O_4) nanoparticles. Then, CM-β-CD modified onto the surface of the nanoparticles can be crosslinked in alkali environment by using EP as a crosslinking agent for abundant exterior hydroxyl groups. The formed cross-linked CM-β-cyclodextrin polymer (CM-β-CDP) layer capsulated around the surface of magnetite nanoparticles can efficiently prevents magnetite nanoparticles from aggregation and oxidation. In addition, CM-β-CDP has superior capabilities for preferable inclusion ability, stability and chemical modification compared to β-CD [31, 32]. Therefore, the superparamagnetic β-CD-functionalized composite nanoparticles with core–shell structures can be anticipated to have a wide variety of biomedical and chemical applications as a very prospective targeting drug carrier and separator for specified substances.

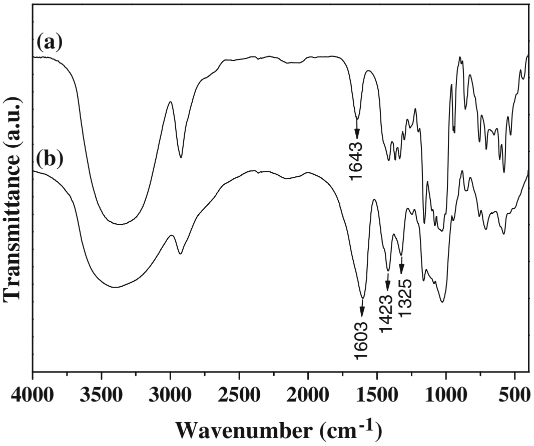


Fig. 1 FTIR spectra of β-CD (*a*) and CM-β-CD (*b*)

Experimental

Chemicals and materials

Monochloroacetic acid of analytical grade and EP were obtained from Shanghai Jingchun Chemical Co. Ltd. β-cyclodextrin of reagent grade (Shanghai Boao Biotech Co. Ltd) was recrystallized twice from de-ionized water and dried in vacuo at 95 °C for 24 h before use. Ferric chloride ($FeCl_3{\cdot}6H_2O$), ferrous sulphate ($FeSO_4{\cdot}7H_2O$) and ammonium hydroxide ($NH_3{\cdot}H_2O$, 25%) were obtained from Guangzhou Chemical Reagents Company and used without further purification. Sodium hydroxide and methanol was procured from Chongqing Hongyan Chemical Co. Ltd. The double distilled water was used throughout this study and a permanent magnet was obtained locally and utilized to separate magnetite nanoparticles.

Synthesis of carboxymethyl β-cyclodextrin

Carboxymethyl β-CD was synthesized following the procedure introduced by a literature as reference via nucleophilic substitution reaction of β-CD and monochloroacetic acid in alkaline media reported by Junge Zhi et al. [33]

$$\beta\text{-CD}{-}\text{OH} + \text{OH}^- \rightarrow \beta\text{-CD}{-}\text{O}^- + \text{H}_2\text{O}$$

$$\beta\text{-CD}{-}\text{O}^- + \text{Cl}{-}\text{CH}_2\text{COOH} \rightarrow \beta\text{-CD}{-}\text{O}{-}\text{CH}_2\text{COOH} + \text{Cl}^-$$

The optimum detailed synthesis procedure of the preparation obtained through experiments that we recommend was as following: predetermined β-CD and NaOH dissolved in distilled water, then, monochloroacetic acid with mole ratio 6:1 to β-CD was added. The mixture was stirred at 80 °C for 4 h, cooled to room temperature and its pH value was adjusted to 4–6 by using hydrochloric acid. Then it was washed with ethanol/water (80/20) solution repeatedly until no Cl^{-1} was detected by using $AgNO_3$ as a detect reagent. The obtained solution without Cl^{-1} was mixed with a large amount of methanol and white precipitation produced. The solid precipitation was filtrated and dried at 70 °C under vacuum for 3 days. The final yield was calculated to be 86.2% and the carboxymethylated degree 4.9 was determined by a method of titrating carboxylate group with perchloric acid in acetic acid.

Preparation of magnetite nanoparticles

The magnetite nanoparticles were prepared by traditional chemical co-precipitation method. Predetermined amounts of $FeCl_3{\cdot}6H_2O$ and $FeSO_4{\cdot}7H_2O$ were dissolved in distilled water under intense stirring at 55 °C and under N_2 atmosphere. Subsequently, chilled NH_4OH was added and the stirring was kept at 800 rpm for 0.5 h ($Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$). The formed magnetite nanoparticles after the reaction were deposited with a permanent magnet placed under the reaction flask and supernatant liquid was removed. The particles were washed with distilled water repeatedly and dried for 24 h at room temperature in a vacuum oven.

Surface modification of magnetite nanoparticles

Predetermined amount of magnetite nanoparticles were added to 50 mL aqueous solution of 1.0 g CM-β-CD. After ultrasonic treatment at 80 °C for 1 h, the mixture was cooled down to room temperature and washed several times with distilled water to remove excess CM-β-CD. After drying at room temperature in a vacuum oven, magnetite nanoparticles modified by CM-β-CD were obtained.

Preparation of β-cyclodextrin-functionalized composite nanoparticles

The CM-β-CD modified magnetite nanoparticles were added to dilute NaOH aqueous solution. After ultrasonic dispersion for 20 min, stable magnetic fluid was obtained. Predetermined amount of EP was added into the magnetic fluid and the mixture was stirred in a three-necked flask for 24 h at 80 °C in N_2 atmosphere for cross-linking reaction. The mixture was cooled down to room temperature and its pH value was adjusted to 4–6 by using hydrochloric acid. The obtained composite nanoparticles were washed with distilled water and separated with a magnetic repeatedly. The final product was dried for 24 h at 70 °C in a vacuum oven.

Characterization

The CM-β-CD sample was analyzed by Fourier transform infrared (FTIR) spectroscopy which was performed on a MAGANA-IR760 spectrometer using potassium bromide pressed disc method, with 2 cm^{-1} resolution and 32 scanning times. The structures of the prepared composite nanoparticles were studied by FTIR spectroscopy and an X-ray diffractometer (D/max-IIIA, Japan) equipped with a graphite homochromatic instruments and Cu anticathode (30 kV, 30 mA, scanning rate 2°/min, $2\theta = 10°–80°$). The morphology of the magnetite nanoparticles and the composite nanoparticles in aqueous solution were observed with a high resolution transmission electron microscope (Hitachi-JEM-100CX II, Japan). The samples were ultrasonicated for 30 min in advance and sprayed onto a Cu grid for observation with an accelerating voltage of 100 kV. The thermal degradation behaviour of the composite nanoparticles was tested using thermo-gravimeter (Netzsh TG-200PC, Germany) in combination with a TA System Controller. The N_2 flow rate was 40 mL/min, and the heating rate was 10 °C/min. The magnetic properties of the composite nanoparticles were measured by vibrating sample magnetometry (VSM) (Lake Shore 7410, US) at 298 K. Spectrophotometer (UV2-200, Japan) was utilized to check the inclusive ability of the composite nanoparticles by testing the concentration variation of naphthalene (NA) ethanol/water (20/80) solution according to the amount of the prepared composite nanoparticles which can be anticipated to form complexes with NA molecules and be removed from the mixture of NA ethanol/water (20/80) solution and the composite nanoparticles with an external magnetic field before spectrophotometric determination. The wavelength used to determine the concentration of NA is 221 nm.

Results and discussion

FTIR analysis of the CM-β-CD sample

Figure 1 shows the FTIR spectra of β-CD (a) and synthesized CM-β-CD sample (b) utilized as coating surfactant of magnetite nanoparticles. The absorption bands at 3416 and 2928 cm^{-1} in Fig. 1a are attributed to the stretching vibrations of alcoholic O–H groups and C–H groups in β-CD, respectively. The absorption bands at 1643, 1371, 1157, 1082 and 1017 cm^{-1} are in correspond to symmetric stretching vibrations and asymmetric stretching vibrations of C–O groups in β-CD. Compared with Fig. 1a, newly appeared absorption bands at 1603, 1423 and 1325 cm^{-1} in Fig. 1b corresponding to $-COO^-$ groups and intensity reduction of absorption bands at 3416 cm^{-1} corresponding to alcoholic O–H groups which is ascribed to the partial substitution of hydroxyl by carboxymethyl confirmed the carboxymethylation of β-CD with the degree of substitution about 4.9 determined by a method of titrating carboxylate group with perchloric acid in acetic acid.

FTIR analysis of β-cyclodextrin-functionalized composite nanoparticles

Figure 2 shows the FTIR spectra of unmodified magnetite nanoparticles (a), the prepared composite nanoparticles (b) and CM-β-CD polymer (c) which were prepared with the same cross-linking agent and almost under the same cross-linking conditions. For both unmodified magnetite nanoparticles and composite nanoparticles, the strong characteristic absorption bands of magnetite at around 586 cm^{-1} are clearly visible in the spectra. Compared with unmodified magnetite nanoparticles in Fig. 2a, the prepared composite nanoparticles in Fig. 2b present newly appeared absorption bands at 1125, 1039 and 2936 cm^{-1} corresponding to –CO, C–O–C and C–H bonds in CM-β-CD polymer in Fig. 2c, respectively. This indicates that β-CD moiety has been combined with magnetite nanoparticles successfully.

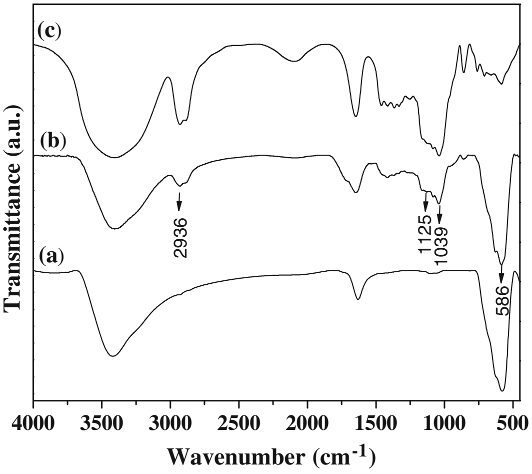


Fig. 2 FTIR spectra of unmodified magnetite nanoparticles (*a*), β-CD-functionalized composite nanoparticles (*b*) and CM-β-CD polymer (*c*)

X-ray diffraction analysis of β-cyclodextrin-functionalized composite nanoparticles

The crystalline structures of unmodified magnetite nanoparticles and the prepared composite nanoparticles were studied by X-ray diffraction (XRD) measurement. It can be found that the crystalline patterns of both nanoparticles coincided very well with standard pattern of magnetite (Fe_3O_4) from the JCPDS card (19-0629), showing an isometric-hexoctahedral crystal system. The diffraction peaks at 30.1°, 43.2°, 57.1° and 62.7° of the composite nanoparticles were similar to those of unmodified magnetite nanoparticles. This indicates that the outer shell of CM-β-CD polymer did not change the typical XRD pattern of magnetite. Such a crystal system was important for superior superparamagnetic properties to be maintained. The relatively broader peaks of the composite nanoparticles in Fig. 3b than those of unmodified magnetite nanoparticles in Fig. 3a suggest that magnetite in the composite nanoparticles have better nanocrystallite nature which is attributed to the barrier effect of outer shell of β-CD polymer from aggregation and oxidation of magnetite nanoparticles.

Structure and morphology of β-cyclodextrin-functionalized composite nanoparticles

Transmission electron microscope (TEM) was used to obtain direct information about the structure and morphology of the prepared composite nanoparticles. The sample for TEM was prepared by dropping dispersions of unmodified magnetite nanoparticles and the composite nanoparticles in aqueous solution onto carbon-coated copper grids after sonication and drying under vacuum. Figure 4 shows the TEM images of the unmodified magnetite nanoparticles and the prepared composite nanoparticles. It can be seen that the unmodified magnetite nanoparticles in Fig. 4a are approximately 10 nm in diameter and trend to agglomerate because some

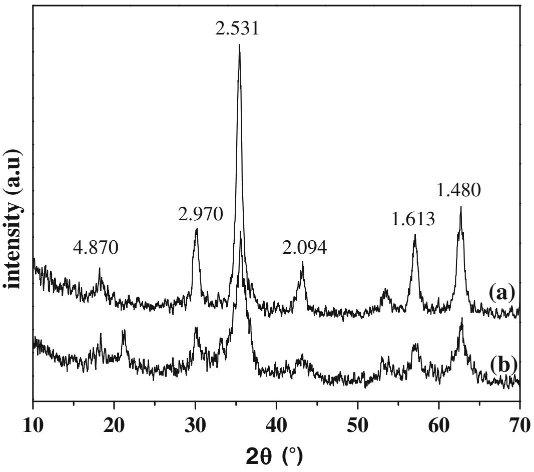


Fig. 3 XRD patterns of unmodified magnetite nanoparticles (*a*) and β-CD-functionalized composite nanoparticles (*b*)

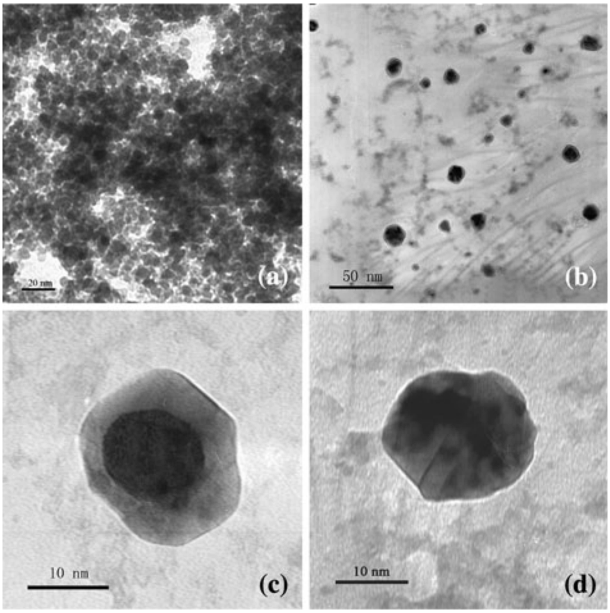
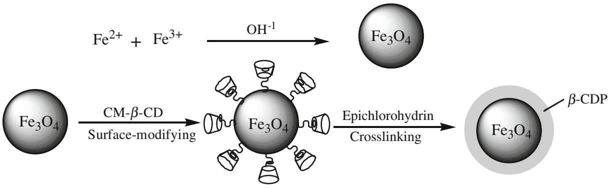


Fig. 4 TEM images of unmodified magnetite nanoparticles (**a**) and β-CD-functionalized composite nanoparticles (**b**, **c**, **d**)

formed big aggregations with tight structure can be observed. Compared to Fig. 4a and b shows a much better dispersion state of the composite nanoparticles in aqueous solution with various sizes in diameter from 10 to 20 nm and the composite nanoparticles display roughly spherical shapes. From Fig. 4c and d, a typical core–shell structure of composite nanoparticles consisting of single magnetite core or multiple cores and an outer layer of CM-β-CD polymer capsulated around the magnetite nanoparticles can be obviously observed. The results agreed well with the designed structure shown in Scheme 1 proposed in the 'Introduction'.

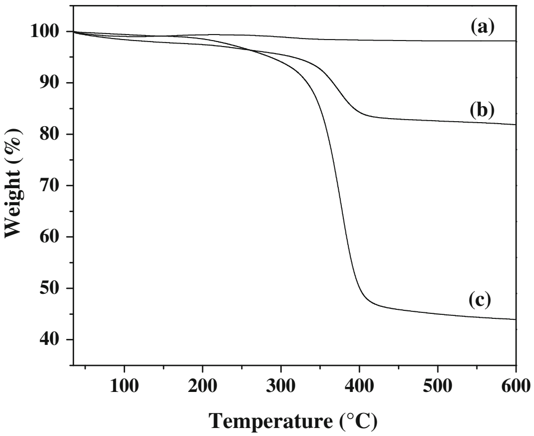
Thermogravimetric analysis of β-CD-functionalized composite nanoparticles

The content of cross-linked CM-β-CD polymer moiety in the prepared composite nanoparticles and the thermal stability were evaluated by thermogravimetric



Scheme 1 Illustration of preparation steps for superparamagnetic β-CD-functionalized composite nanoparticles

Fig. 5 TGA curves of unmodified magnetite nanoparticles (*a*), β-CD-functionalized composite nanoparticles (*b*) and cross-linked CM-β-CD polymer (*c*)



analysis (TGA) technique. Figure 5 presents the thermal degradation curves for unmodified magnetite nanoparticles (a), the prepared composite nanoparticles (b) and CM-β-CD polymer (c) which was prepared with the same cross-linking agent and almost under the same cross-linking conditions. As shown in Fig. 5a, the total weight loss over the full temperature range for unmodified magnetite nanoparticles is about 1.6% due to the loss of the dehydration of the surface hydroxyl groups. For pure CM-β-CD polymer in Fig. 5c, the mass loss of about 55.2% by weight in the range of 200–430 °C is attributed to the decomposition of pure CM-β-CD polymer and the temperature of the maximum weight loss is 378 °C. For the composite nanoparticles in Fig. 5b, the relatively slow weight loss below 200 °C is owing to the loss of residual water absorbed in the cavities of the cross-linked CM-β-CD polymer. Then, well-defined mass weight loss of about 16.3% between 200 and 430 °C can be observed due to the degradation of cross-linked CM-β-CD polymer moiety and the temperature of the maximum weight loss is 376 °C, almost similar to that of pure CM-β-CD polymer. From the above data, a proximate CM-β-CD polymer moiety content of about 29.5% by weight was deduced for the prepared composite nanoparticles.

Evaluation of the magnetic properties of β-cyclodextrin-functionalized composite nanoparticles

The magnetic properties of the prepared composite nanoparticles were investigated by VSM. Figure 6 shows magnetic hysteresis loops of unmodified magnetite nanoparticles (a) and the prepared composite nanoparticles (b) in an applied magnetic field of 20000 Oe at 298 K. The results show that unmodified magnetite nanoparticles and the prepared composite nanoparticles have very low coercive forces of 12.5 and 8.3 Oe, respectively. In addition, nearly no remnant magnetism is left after removal of the applied magnetic field. The hysteresis loops of the prepared composite nanoparticles show typical characters of superparamagnetic behaviour which implies their re-dispersion ability in solution without occurrence of severe aggregation. The saturation magnetization of the composite nanoparticles in Fig. 6b

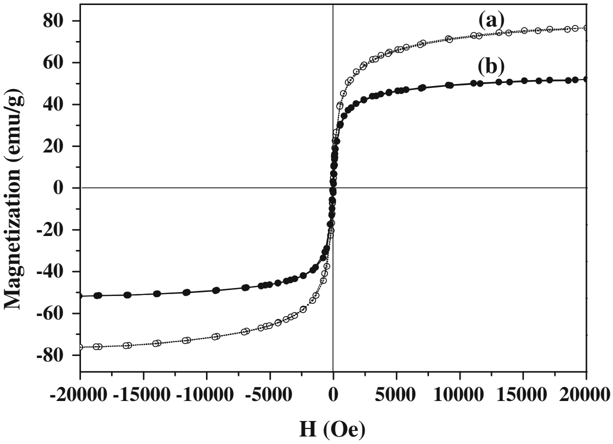


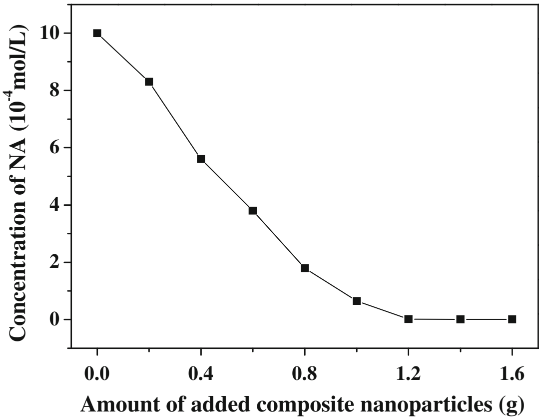
Fig. 6 Magnetic hysteresis loops of unmodified magnetite nanoparticles (*a*) and *β*-CD-functionalized composite nanoparticles (*b*)

is about 52.0 emu/g, relatively lower than that of unmodified magnetite nanoparticles in Fig. 6a because of the contained non-magnetic cross-linked CM-*β*-CD polymer moiety.

Study of the inclusive behaviour of *β*-CD-functionalized composite nanoparticles

The inclusive behaviour of the prepared composite nanoparticles can be studied by analyzing the concentration variation of predetermined amount of NA aqueous-alcohol solution according to the amount of added *β*-CD-functionalized composite nanoparticles which were firstly mixed with predetermined NA aqueous-alcohol (80/20) solution for 24 h and then separated from the mixture with a permanent magnet before concentration determination by means of a spectrophotometer. From Fig. 7, we can find that the concentration of NA aqueous-alcohol solution decreased

Fig. 7 Effect of the amount of added *β*-CD-functionalized composite nanoparticles on the concentration of NA aqueous-alcohol (80/20) solution



as the amount of composite nanoparticles added into the NA aqueous-alcohol solution increased. It indicates that the prepared composite nanoparticles can form complexes with NA molecules through inclusion interaction and a maximum inclusion amount of NA by the composite nanoparticles was deduced as about 0.1 mg/g.

Conclusions

In summary, we developed an original and ideal approach for the feasible preparation of β-CD-functionalized composite nanoparticles possessing both superparamagnetism and functionality of β-CD unit in this study. The composite nanoparticles were prepared successfully via cross-linking reaction of CM-β-CD utilized as a surface-modifier of magnetite nanoparticles by using EP as a cross-linking agent. The size of the prepared composite nanoparticles with roughly spherical shapes and core–shell structures was about 10–20 nm in diameter. The amount of β-CD polymer capsulated around the magnetite nanoparticles in the prepared composite nanoparticles was estimated to be 29.5% by weight. The results of VSM indicated that the composite nanoparticles performed superparamagnetic behaviour and the saturation magnetization was measured to be 52.0 emu/g in an applied magnetic field of 20000 Oe at 298 K. The inclusive ability of the composite nanoparticles was confirmed by studying the inclusion reaction between the composite nanoparticles and NA molecules in aqueous-alcohol solution and a maximum inclusion amount of about 0.1 mg/g was deduced. The composite nanoparticles may have a wide variety of biomedical and chemical applications as a very prospective drug carrier and separator for specified substances.

References

1. Szejitli J (1998) Introduction and general overview of cyclodextrin chemistry. Chem Rev 98:1743–1753
2. Dodziuk H (2006) Cyclodextrins and their complexes: chemistry, analytical methods applications. Wiley-VCH, New York
3. Davis ME, Brewster ME (2004) Cyclodextrin-based pharmaceutics: past, present and future. Nat Rev Drug Discov 3:1023–1035
4. Szejitli J (1998) Cyclodextrin technology, 1st edn. Kluwer Academic Press, Dordrecht, pp 79–81
5. Harada A, Furue M, Nozakura SI (1976) Cyclodextrin-containing polymers: 1. Preparation of polymers. Macromolecules 9:701–704
6. Harada A, Furue M, Nozakura SI (1977) Interaction of cyclodextrin-containing polymers with fluorescence compounds. Macromolecules 10:676–681
7. Sreenivasan K (1997) On the restriction of the release of water-soluble component from polyvinyl alcohol film by blending β-cyclodextrin. J Appl Polym Sci 65:1829–1832
8. Harada A, Furue M, Nozakura SJ (1978) Optical resolution of mandelic acid derivatives by column chromatography on crosslinked cyclodextrin gels. Polym Sci Polym Chem Ed 16:189–196
9. He BL, Zhao X (1992) Synthesis of novel beta-cyclodextrin polymer. Sci China (Ser B) 12:1240–1247
10. Crini G, Janus L, Morcellet M, Torri G, Naggi A, Bertini S, Vecchi C (1998) Macroporous polyamines containing cyclodextrin: synthesis, characterization, and sorption properties. J Appl Polym Sci 68:1973–1978

11. Hanessian S, Benalil A, Laferriers C (1995) The synthesis of functionalized cyclodextrins as scaffolds and templates for molecular diversity, catalysis, and inclusion phenomena. J Org Chem 60:4786–4797
12. Mosbach K, Andersson L (1977) Magnetic ferrofluids for preparation of magnetic polymers and their application in affinity chromatography. Nature 270:259–261
13. Pinho MS, Gregori ML, Nunes RCR, Soares BG (2001) Aging effect on the reflectivity measurements of polychloroprene matrices containing carbon black and carbonyl-iron powder. Polym Degrad Stab 73:1–5
14. Katz E, Weizmann H, Willner I (2005) Magnetoswitchable reactions of DNA monolayers on electrodes: gating the processes by hydrophobic magnetic nanoparticles. J Am Chem Soc 17:9191–9200
15. Cheng GF, Zhao J, Tu YH, He PG, Fang YZ (2005) A sensitive DNA electrochemical biosensor based on magnetite with a glassy carbon electrode modified by muti-walled carbon nanotubes in polypyrrole. Anal Chim Acta 533:11–16
16. Jain TK, Roy I, De TK, Maitra A (1998) Nanometer silica particles encapsulating active compounds: a novel ceramic drug carrier. J Am Chem Soc 120:11092–11095
17. Aoyama Y, Kanamori T, Nakai T, Sasaki T, Horiuchi S, Sando S, Niidome T (2003) Artificial viruses and their application to gene delivery: size-controlled gene coating with glycocluster nanoparticles. J Am Chem Soc 125:3455–3457
18. Dahan M, Levi S, Luccardini C, Rostaing P, Riveau B, Triller A (2003) Diffusion dynamics of glycine receptors revealed by single-quantum dot tracking. Science 302:442–445
19. Cao YC, Jin R, Mirkin CA (2002) Nanoparticles with raman spectroscopic fingerprints for DNA and RNA detection. Science 297:1536–1540
20. Lai C, Trewyn BG, Jeftinija DM, Jeftinija K, Xu S, Jeftinija S, Lin VS (2003) A mesoporous silica nanosphere-based carrier system with chemically removable CdS nanoparticle caps for stimuli-responsive controlled release of neurotransmitters and drug molecules. J Am Chem Soc 125:4451–4459
21. Berensmeier S (2006) Magnetic particles for the separation and purification of nucleic acids. Appl Microbiol Biotechnol 73:495–504
22. Cornell RM, Schwertmann U (1996) The iron oxides. Verlagsgesellschaft VCH, Weinheim
23. Hunter RJ (1987) Foundations of colloid science, vol I. Clarendon Press, Oxford
24. Shi DL, He P (2004) Surface modifications of nanoparticles and nanotubes by plasma polymerization. Rev Adv Mater Sci 7:97–107
25. Gupta AK, Wells S (2004) Surface-modified superparamagnetic nanoparticles for drug delivery: preparation, characterization, and cytotoxicity studies. IEEE Trans Nanobiosci 3:66–73
26. Kumar RV, Koltypin Y, Cohen YS, Cohen Y, Aurbach D, Palchik O, Felner I, Gedanken A (2000) Preparation of amorphous magnetite nanoparticles embedded in polyvinyl alcohol using ultrasound radiation. J Mater Chem 10:1125–1129
27. Cao HN, He J, Deng L, Gao XQ (2009) Fabrication of cyclodextrin-functionalized super-paramagnetic Fe_3O_4/amino-silane core–shell nanoparticles via layer-by-layer method. J Appl Surf Sci 255:7974–7980
28. Banerjee SS, Chen DH (2009) Cyclodextrin-conjugated nanocarrier for magnetically guided delivery of hydrophobic drugs. J Nanopart Res 11:2071–2078
29. Banerjee SS, Chen DH (2007) Magnetic nanoparticles grafted with cyclodextrin for hydrophobic drug delivery. Chem Mater 19:6345–6349
30. Xia HB, Yi JB, Foo PS, Liu BH (2007) Facile fabrication of water-soluble magnetic nanoparticles and their spherical aggregates. Chem Mater 19:4087–4091
31. Martel B, Leckchiri Y, Pollet A, Morcellet M (1995) Cyclodextrin-poly(vinylamine) systems-I. Synthesis, characterization and conformational properties. Eur Polym J 31:1083–1088
32. Xu WY, Demas JN, Degraff BA, Whaley M (1993) Interactions of pyrene with cyclodextrins and polymeric cyclodextrins. J Phys Chem 97:6546–6554
33. Zhi JG, Tian XL, Zhao W, Shen JB, Tong B, Dong YP (2008) Self-assembled film based on carboxymethyl-beta-cyclodextrin and diazoresin and its binding properties for methylene blue. J Colloid Interface Sci 319:270–276