



# Influence of chitosan modification on self-assembly behavior of Fe<sub>3</sub>O<sub>4</sub> nanoparticles

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## Abstract

Self-assembled Fe<sub>3</sub>O<sub>4</sub> nanoparticles are attracting more and more interests in biomedical field, such as dual photoacoustic devices and magnetic resonance imaging. At present, however, the preparation of self-assembled Fe<sub>3</sub>O<sub>4</sub> nanoparticles mainly relies on the modifications of some toxic polymers, such as 4-vinylpyridine, polyacrylonitrile, and phenol formaldehyde resin. Additionally, the synthetic methods used were too complicated. The biological toxicity and complex methods significantly limit the biomedical applications of self-assembled Fe<sub>3</sub>O<sub>4</sub> nanoparticles. In this work, natural polysaccharide chitosan was used to modify Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The self-assembled Fe<sub>3</sub>O<sub>4</sub> nanochains were obtained easily by controlling the ratio of chitosan and Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The formation mechanism of Fe<sub>3</sub>O<sub>4</sub> nanochains was proposed and demonstrated by experiments and numerical simulation. It is found that the thickness of chitosan is a key factor that affects the magnetic field distributions and magnetic attraction of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The prepared chitosan-modified Fe<sub>3</sub>O<sub>4</sub> nanochains would be a promising candidate with good biocompatibility for biomedical applications.

**Keywords** Fe<sub>3</sub>O<sub>4</sub> nanoparticle · Chitosan · Self-assembly · Magnetic materials

## Introduction

In the past decade, self-assembly has emerged as a very attractive method for constructing ordered nanostructures, due to its scalability and simplicity (Lin et al. 2016; Berrod et al. 2015). Magnetic nanoparticles, which have unique properties for many applications especially in biomedical areas (Zou et al. 2018; Vergaro et al. 2011; Parekh et al. 2018; Lvov et al. 2011; Gao et al. 2020), are excellent building blocks for self-assembly (Li et al. 2018).

Magnetite (Fe<sub>3</sub>O<sub>4</sub>), as one of the most important magnetic materials with promising applications in numerous field (Wan et al. 2007; Wang et al. 2007), has received considerable attention in the study of self-assembled magnetic nanoparticles (Gong et al. 2010). With the efforts of many researchers, self-assembled Fe<sub>3</sub>O<sub>4</sub> nanochains with various lengths and different shapes have been reported (Gong et al. 2010; Zhang et al. 2009; Kim et al. 2014). Song et al. designed a new model of vesicles assembled by “Janus” Au–Fe<sub>3</sub>O<sub>4</sub> nanoparticles grafted with different hydrophilicity polymer on Au and Fe<sub>3</sub>O<sub>4</sub> surfaces separately, and used the vesicles for dual photoacoustic and magnetic resonance imaging in vivo (Song et al. 2017). Although constructing various self-assembled Fe<sub>3</sub>O<sub>4</sub> nanostructures has achieved

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great success (Zhang et al. 2007), the methods applied are complicated and the polymers used are mostly toxic. Therefore, developing a facile method with nontoxic polymer for constructing self-assembled  $\text{Fe}_3\text{O}_4$  nanostructures is still highly desired.

Chitosan, which is an abundant biopolymer extracted from crab and shrimp shells (Gortari and Hours 2013; Kandara et al. 2012), has attracted particular attention in a wide variety of fields because it is biocompatible, biodegradable, antimicrobial, environment friendly, and low cost (Silva et al. 2017; Sun et al. 2017; Verlee et al. 2017). Moreover, chitosan has a special characteristic of pH-sensitivity (Solubility decreases with increasing pH value), which may provide a new strategy to synthesize chitosan complex by adjusting the pH value.

Inspired by these promises, we have developed an efficient dissolution–precipitation route for the large-scale synthesis of self-assembled chitosan-modified  $\text{Fe}_3\text{O}_4$  nanochains, which is different from the previous reports. The microstructure and magnetic properties of the as-synthesized  $\text{Fe}_3\text{O}_4$  nanochains have been studied. Moreover, the formation mechanism of  $\text{Fe}_3\text{O}_4$  nanochains have been proposed and demonstrated. The as-synthesized chitosan-modified  $\text{Fe}_3\text{O}_4$  nanochains may be a promising candidate in biomedical applications, such as bio self-healing (Seifan et al. 2018), nucleic acid extraction (Oster et al. 2001), DNA detection (Wang et al. 2001) and protein–protein interaction (Schotte et al. 2012).

## Materials and methods

### Synthesis of $\text{Fe}_3\text{O}_4$ nanoparticles

0.4 g iron (III) chloride anhydrous ( $\text{FeCl}_3$ , Sinopharm Chemical Reagent Co., China), 3.2 g sodium acetate anhydrous ( $\text{CH}_3\text{COONa}$ , Tianjin Kermel Chemical Reagent Co., China) and 0.8 g polyethylene glycol 1000 (PEG, Sinopharm Chemical Reagent Co., China) were dispersed in 35 mL ethylene glycol ( $(\text{CH}_2\text{OH})_2$ , Sinopharm Chemical Reagent Co., China) with stirring magnetically for 30 min. Then, the mixed solution were transferred into a 50 mL Teflon autoclave, heated to 180 °C and maintained for 16 h. After cooling to room temperature, the products were taken out and washed by ethanol and distilled water for several times.

### Modification of chitosan

25 mg chitosan was dissolved in 17.25 mL distilled water with the presence of 250  $\mu\text{L}$  acetic acid ( $\text{CH}_3\text{COOH}$ , Tianjin Kermel Chemical Reagent Co., China). 250 mg as-prepared  $\text{Fe}_3\text{O}_4$  nanoparticles were dispersed in the mixed solution with stirring magnetically for 30 min. 1 mL ammonia

solution ( $\text{NH}_4\text{OH}$ , Tianjin Kermel Chemical Reagent Co., China) was then added. After vigorous stirring for 24 h, the products were washed by ethanol and distilled water for several times and dried at 60 °C for 6 h. For comparison,  $\text{Fe}_3\text{O}_4$  nanoparticles without chitosan modification and  $\text{Fe}_3\text{O}_4$  nanoparticles modified with 75 mg chitosan were also prepared by the same method. We labeled the  $\text{Fe}_3\text{O}_4$  nanoparticles without chitosan modification,  $\text{Fe}_3\text{O}_4$  nanoparticles modified with chitosan of 25 mg and 75 mg as  $\text{Fe}_3\text{O}_4-1$ ,  $\text{Fe}_3\text{O}_4-2$  and  $\text{Fe}_3\text{O}_4-3$ , respectively.

## Characterization

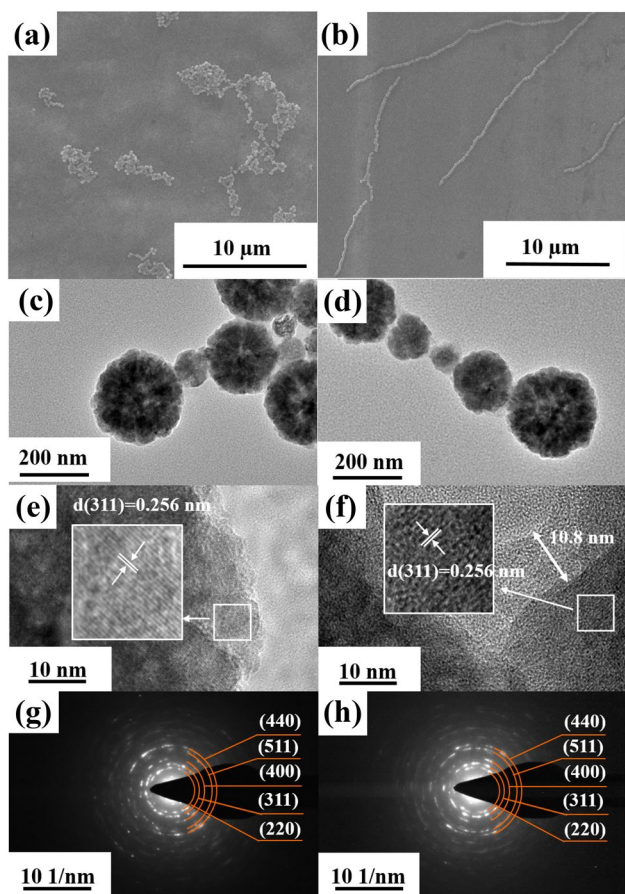
The morphology of the as-synthesized nanoparticles was characterized by scanning electron microscopy (SEM, FEI, QUANTA 450) and transmission electron microscopy (TEM, FEI, Tecnai F30). The crystal structure of nanoparticles was investigated by X-ray diffraction (XRD, Empyrean with  $\text{Cu-K}\alpha$  radiation). Magnetic properties were studied by vibrating sample magnetometry (VSM, LDJ Electronics Inc., Model 9600). The chitosan content was investigated by Fourier transform infrared spectrophotometer (FTIR, Bruker, EQUINOX55) and thermogravimetric analysis (TGA, Perkin Elmer Instruments model, STA 6000).

## Results and discussion

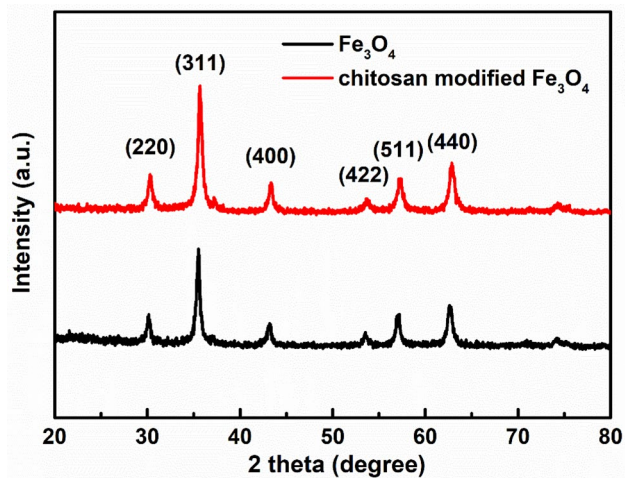
The morphology of pristine  $\text{Fe}_3\text{O}_4$  nanoparticles and chitosan-modified  $\text{Fe}_3\text{O}_4$  nanoparticles are characterized by SEM and TEM images. It is observed from Fig. 1a that the pristine  $\text{Fe}_3\text{O}_4$  nanoparticles agglomerate together disorderly due to their high surface energy and magnetic attraction. After the modification of chitosan (Fig. 1b),  $\text{Fe}_3\text{O}_4$  nanoparticles are assembled to nanochains with several micrometers in length.

Figure 1c shows the typical TEM image of pristine  $\text{Fe}_3\text{O}_4$  nanoparticles with sizes ranging from 100 to 300 nm. The HRTEM image in Fig. 1e shows the lattice parameter of 0.256 nm is consistent with the (311) plane in spinel magnetite. Figure 1d, f are TEM images of the chitosan-modified  $\text{Fe}_3\text{O}_4$  nanoparticles. After adding chitosan, a uniform coating on an entire nanoparticle surface with an average thickness of 10.8 nm is formed. Figure 1g, h are the selected area electron diffraction patterns of a pristine  $\text{Fe}_3\text{O}_4$  nanoparticle and a chitosan-modified  $\text{Fe}_3\text{O}_4$  nanoparticle, respectively. Five obvious diffraction rings match well with standard spinel  $\text{Fe}_3\text{O}_4$  diffraction pattern.

XRD has been used to investigate the crystal structure of nanoparticles, and the obtained XRD patterns are shown in Fig. 2. All peaks can be indexed to the standard spinel structure (JCPDS No. 01-1111), and no peaks from impurities are found.



**Fig. 1** SEM images of **a** pristine Fe<sub>3</sub>O<sub>4</sub> nanoparticles and **b** chitosan-modified Fe<sub>3</sub>O<sub>4</sub> nanochains; TEM images of **c** pristine Fe<sub>3</sub>O<sub>4</sub> nanoparticles and **d** chitosan-modified Fe<sub>3</sub>O<sub>4</sub> nanochains; HRTEM images of **e** pristine Fe<sub>3</sub>O<sub>4</sub> nanoparticles and **f** chitosan modified Fe<sub>3</sub>O<sub>4</sub> nanochains; selected area electron diffraction patterns of **g** pristine Fe<sub>3</sub>O<sub>4</sub> nanoparticles and **h** chitosan-modified Fe<sub>3</sub>O<sub>4</sub> nanochains

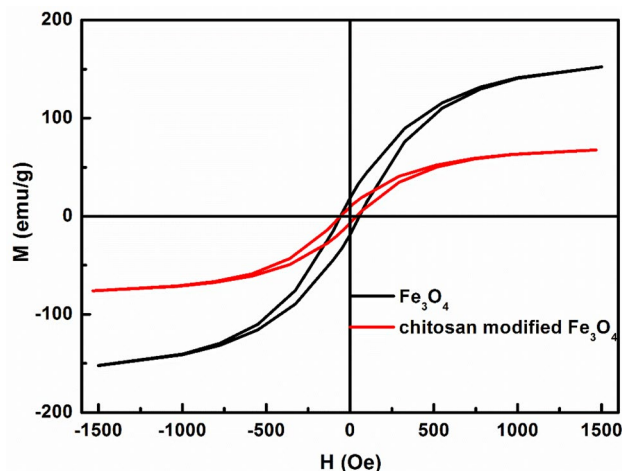


**Fig. 2** XRD patterns of the pristine Fe<sub>3</sub>O<sub>4</sub> nanoparticles and the chitosan-modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles

The magnetic properties of the pristine Fe<sub>3</sub>O<sub>4</sub> nanoparticles and the chitosan-modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles are studied by VSM, and the hysteresis loops are given in Fig. 3. The coercivity *H<sub>c</sub>* and saturation magnetization *M<sub>s</sub>* for the chitosan-modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles are 49 Oe and 68 emu/g, respectively, which are lower than those for pristine Fe<sub>3</sub>O<sub>4</sub> nanoparticles (*H<sub>c</sub>* = 58 Oe, *M<sub>s</sub>* = 152 emu/g). The decrease of *M<sub>s</sub>* mainly attributes to the addition of nonmagnetic chitosan, which reduces the magnetic moments per unit mass.

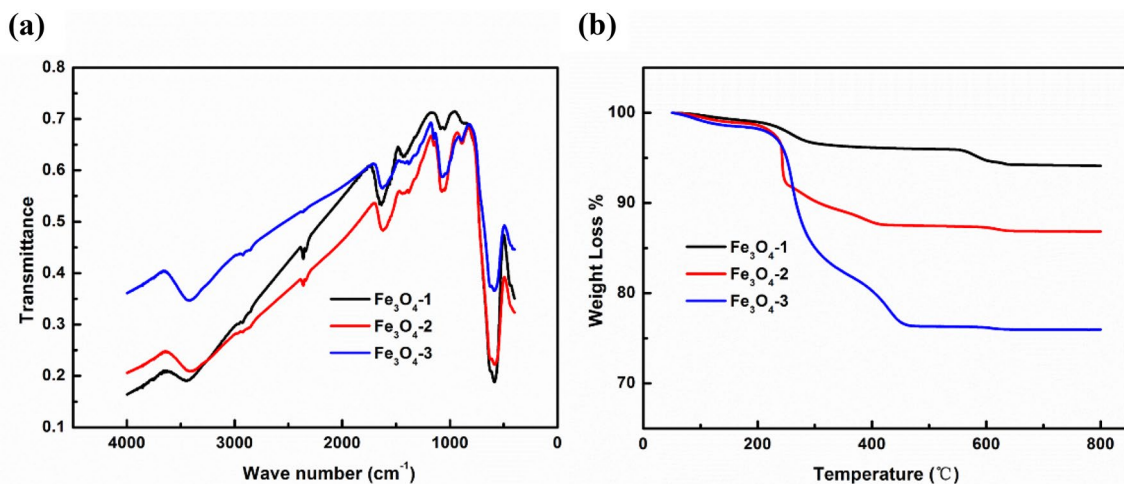
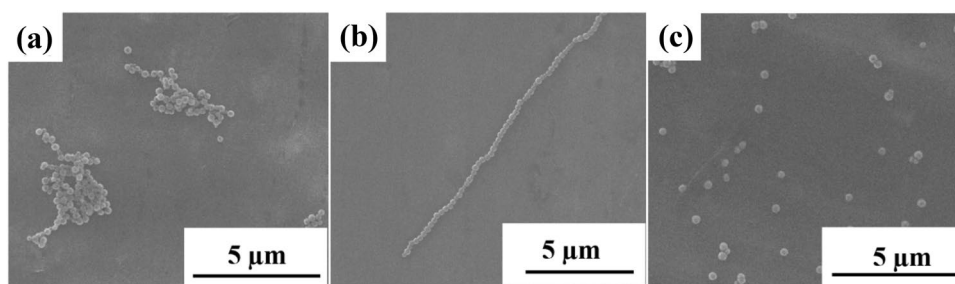
To investigate the influence of chitosan content on the aggregation states of Fe<sub>3</sub>O<sub>4</sub> nanoparticles, Fe<sub>3</sub>O<sub>4</sub> nanoparticles with three different chitosan contents are prepared. Figure 4a shows that Fe<sub>3</sub>O<sub>4</sub> – 1 aggregate together randomly due to their strong magnetic interactions. Figure 4b shows that Fe<sub>3</sub>O<sub>4</sub> – 2 tend to form nanochains due to the decreased magnetic interactions. However, when the chitosan content was increased to 75 mg (Fig. 4c), the magnetic field intensity of each Fe<sub>3</sub>O<sub>4</sub> – 3 nanoparticle is too weak to attract the nanoparticles nearby; therefore, most of the Fe<sub>3</sub>O<sub>4</sub> – 3 nanoparticles are separated.

In order to investigate the chitosan contents in the Fe<sub>3</sub>O<sub>4</sub> – 1, Fe<sub>3</sub>O<sub>4</sub> – 2, and Fe<sub>3</sub>O<sub>4</sub> – 3, FTIR and TGA have been carried out. It is found in Fig. 5a that FTIR spectra reveal several characteristic absorption peaks of Fe<sub>3</sub>O<sub>4</sub> and chitosan. The peak observed at 563 cm<sup>-1</sup> is assigned to Fe–O vibration of Fe<sub>3</sub>O<sub>4</sub> component (Rahmanzadeh et al. 2014). For the chitosan component, the peaks at 2835 and 1375 cm<sup>-1</sup> correspond to C–H stretching vibrations, while another peak at 1252 cm<sup>-1</sup> is assigned to C–N vibration (Le VT et al. 2018). As shown in the Fig. 5a, the peak at 563 cm<sup>-1</sup> for Fe<sub>3</sub>O<sub>4</sub> – 1 is stronger than those for Fe<sub>3</sub>O<sub>4</sub> – 2 and Fe<sub>3</sub>O<sub>4</sub> – 3, indicating that Fe<sub>3</sub>O<sub>4</sub> – 1 has the highest Fe<sub>3</sub>O<sub>4</sub> content. It is also found that the peak at 1252 cm<sup>-1</sup> for



**Fig. 3** Hysteresis loops of the pristine Fe<sub>3</sub>O<sub>4</sub> nanoparticles and chitosan-modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles

**Fig. 4** SEM images of  $\text{Fe}_3\text{O}_4$  nanoparticles: **a**  $\text{Fe}_3\text{O}_4-1$ , **b**  $\text{Fe}_3\text{O}_4-2$ , and **c**  $\text{Fe}_3\text{O}_4-3$



**Fig. 5** **a** FTIR spectra of  $\text{Fe}_3\text{O}_4-1$ ,  $\text{Fe}_3\text{O}_4-2$ , and  $\text{Fe}_3\text{O}_4-3$ . **b** TGA curves of the  $\text{Fe}_3\text{O}_4-1$ ,  $\text{Fe}_3\text{O}_4-2$  and  $\text{Fe}_3\text{O}_4-3$

$\text{Fe}_3\text{O}_4-3$  is stronger than those for  $\text{Fe}_3\text{O}_4-1$  and  $\text{Fe}_3\text{O}_4-2$ , showing that  $\text{Fe}_3\text{O}_4-3$  has the highest chitosan content.

Figure 5b shows the TGA curves from room temperature up to 800 °C in air. In the range of 220–420 °C, the weight losses of  $\text{Fe}_3\text{O}_4-2$  and  $\text{Fe}_3\text{O}_4-3$  are about 13.15% and 24.04%, respectively, corresponding to the release of physically adsorbed water and thermal decomposition of the chitosan. For the  $\text{Fe}_3\text{O}_4-1$  sample without chitosan modification, only 5.87% weight loss only due to the adsorbed water is observed. Supposing that the absorbed water are almost the same in the three samples, the chitosan contents in  $\text{Fe}_3\text{O}_4-2$  and  $\text{Fe}_3\text{O}_4-3$  are estimated to be approximately 7% and 18%, respectively.

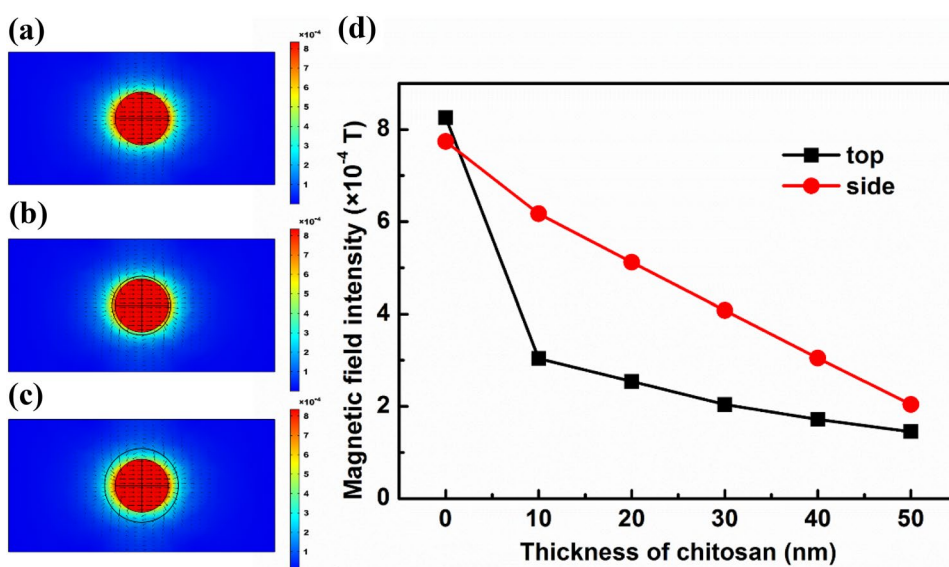
To further verify the experiments, the magnetic field distributions of a single  $\text{Fe}_3\text{O}_4$  nanoparticle with different thicknesses of chitosan are simulated by COMSOL (Comsol Multiphysics software), where the size of  $\text{Fe}_3\text{O}_4$  nanoparticles is set to be 200 nm and the thicknesses of chitosan are set to be 0, 10 and 40 nm. Moreover, since the  $\text{Fe}_3\text{O}_4$  nanoparticles have been magnetized by a magnetic stirring apparatus during the synthesis and modification process; therefore, the magnetic property of each  $\text{Fe}_3\text{O}_4$  nanoparticle is anisotropic. In the simulation, two sides of each nanoparticle were set as two magnetic poles. The magnetic field distributions of

the  $\text{Fe}_3\text{O}_4$  nanoparticles with chitosan layers of 0 nm, 10 nm and 40 nm are shown in Figs. 6a–c, respectively, and the variation of magnetic field intensities at the top and side of each nanoparticle against chitosan thickness is plotted in Fig. 6d. The magnetic field intensity at the top of the single  $\text{Fe}_3\text{O}_4$  nanoparticle without chitosan modification (Fig. 6a, d) is about  $8.26 \times 10^{-4}$  T, which is similar to both sides of the nanoparticles ( $7.74 \times 10^{-4}$  T). Hence, the single  $\text{Fe}_3\text{O}_4$  nanoparticle has almost the same strong magnetic attractions in different directions. This is the reason for the aggregation of the  $\text{Fe}_3\text{O}_4$  nanoparticles.

As the thickness of chitosan increases, both top and side magnetic field intensities of  $\text{Fe}_3\text{O}_4$  nanoparticles decrease. When the thickness of chitosan is 10 nm (Fig. 6b, d), the difference of magnetic field intensities between the top and side of nanoparticles is maximum. The magnetic field intensity at the top part is  $3.04 \times 10^{-4}$  T, which is much weaker than the both sides of the nanoparticles ( $6.17 \times 10^{-4}$  T). Therefore, the other nanoparticles nearby would be attracted by the left or right side of the  $\text{Fe}_3\text{O}_4$  nanoparticles, leading to the formation of nanochains.

When the thickness of chitosan is increased to 40 nm (Fig. 6c, d), however, there is a little difference in magnetic field intensities between the top and side of the particle.

**Fig. 6** Magnetic field distributions of Fe<sub>3</sub>O<sub>4</sub> nanoparticles with different thicknesses of chitosan layers of **a** 0 nm, **b** 10 nm and **c** 40 nm, **d** Magnetic field intensities at the top and the side of Fe<sub>3</sub>O<sub>4</sub> nanoparticles against the thickness of chitosan

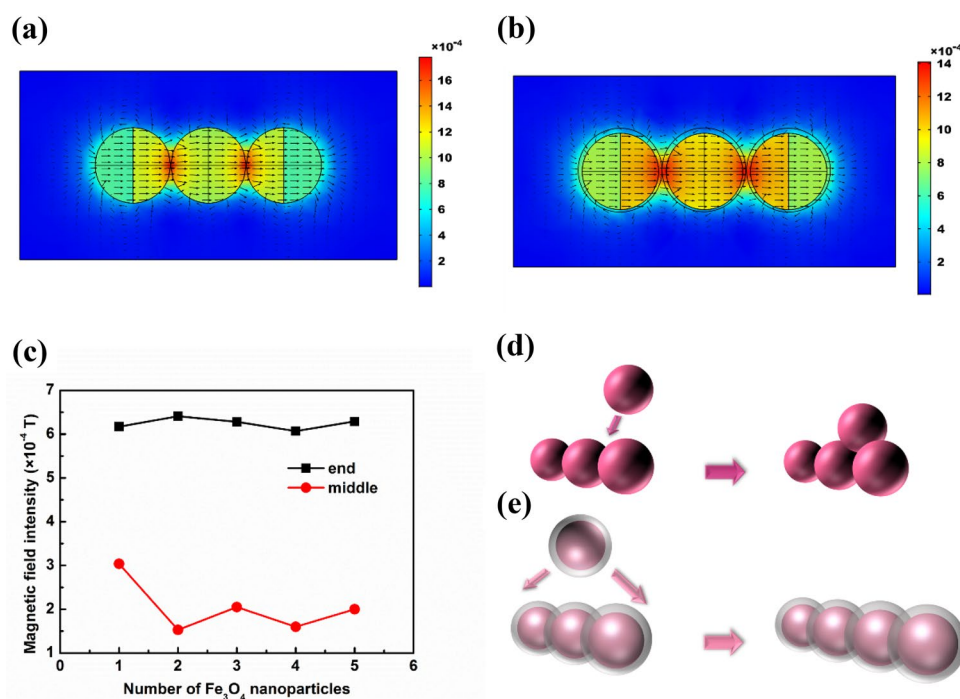


The magnetic field intensity at the top part of particle is decreased to  $1.72 \times 10^{-4}$  T, and that at the both sides also decreased to  $3.05 \times 10^{-4}$  T. Therefore, the magnetic attractions for Fe<sub>3</sub>O<sub>4</sub> nanoparticles with chitosan thickness of 40 nm are very weak even at the both sides of the particles, which is not strong enough to attract other nanoparticles nearby, leading to the distribution of separated nanoparticles. The theoretical simulations agree well with the experiment results.

The magnetic field distributions of nanochains are also simulated by COMSOL, where the size of Fe<sub>3</sub>O<sub>4</sub> nanoparticles

is set to be 200 nm and the chitosan thickness is 10 nm. In Fig. 7a, three Fe<sub>3</sub>O<sub>4</sub> nanoparticles attract each other due to the strong magnetic interactions between magnetic poles. The magnetic field intensity around the middle part of the three particles is about  $8.87 \times 10^{-4}$  T, which is slightly stronger than those at two ends of the Fe<sub>3</sub>O<sub>4</sub> nanochain ( $7.15 \times 10^{-4}$  T). Figure 7d shows when another particle comes to join the group of three particles, there are two possible positions for it to connect: the ends or the middle part of the three Fe<sub>3</sub>O<sub>4</sub> nanoparticles. As there are two contact points at the middle part, the newcomer would be more likely attached in the middle than at

**Fig. 7** The formation mechanism of Fe<sub>3</sub>O<sub>4</sub> nanochains: **a** Magnetic field distribution of a nanochain formed by three pristine Fe<sub>3</sub>O<sub>4</sub> nanoparticles, **b** Magnetic field distribution of a nanochain formed by three chitosan-modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles, and **c** Magnetic field intensities at the end and middle parts of the Fe<sub>3</sub>O<sub>4</sub> nanochains with different number of nanoparticles in the chain, and each Fe<sub>3</sub>O<sub>4</sub> nanoparticle has a chitosan layer of 10 nm, **d** Schematic of the aggregated Fe<sub>3</sub>O<sub>4</sub> nanoparticles, and **e** Schematic of self-assembled chitosan-modified Fe<sub>3</sub>O<sub>4</sub> nanochains



the ends because this is more stable and energetically favorable. Therefore, the nanochains would not be formed.

Figure 7b shows the magnetic field distribution of nanochain formed by three chitosan modified  $\text{Fe}_3\text{O}_4$  nanoparticles with 10 nm chitosan layer, and Fig. 7c shows the magnetic field intensities at the end and middle parts of the nanochain against the nanoparticles number in the chain. All  $\text{Fe}_3\text{O}_4$  nanoparticles in Figs. 7b, c have a chitosan layer of 10 nm. For the chitosan-modified nanoparticles, the magnetic field intensity around the middle part of the three nanoparticles is about  $2.05 \times 10^{-4}$  T, much lower than those at two ends of the nanochain ( $6.28 \times 10^{-4}$  T). Moreover, as shown in Fig. 7c, although the number of  $\text{Fe}_3\text{O}_4$  nanoparticle increases, the magnetic field intensities at the end and middle parts of  $\text{Fe}_3\text{O}_4$  nanochain do not change a lot, and the magnetic field intensity in middle part is much weaker than the ends of the  $\text{Fe}_3\text{O}_4$  nanochain. As shown in Fig. 7e, when another nanoparticle comes, the two ends of the nanochain are the preferential positions to attract it due to the stronger field intensities, leading to the formation of a longer nanochain. These simulation results are consistent with the experimental results.

## Conclusions

The self-assembled  $\text{Fe}_3\text{O}_4$  nanochains have been prepared by controlling the chitosan thickness coated on the surface of  $\text{Fe}_3\text{O}_4$  nanoparticles. Both numerical simulations and experiments demonstrated that the magnetic field intensities at top and side of a single  $\text{Fe}_3\text{O}_4$  nanoparticle decrease with increasing chitosan thickness. As the chitosan thickness changes from 0 to 10 nm and 40 nm, the state of  $\text{Fe}_3\text{O}_4$  nanoparticles goes from aggregation to nanochains and separated ones. Furthermore, when the chitosan thickness is 10 nm, the difference of magnetic field intensities between the top and side of a single  $\text{Fe}_3\text{O}_4$  nanoparticle reaches the maximum, and remains stable although the number of  $\text{Fe}_3\text{O}_4$  nanoparticle is increased. Therefore, coating with 10 nm chitosan layer is the optimum condition for the formation of  $\text{Fe}_3\text{O}_4$  nanochains. The chitosan-modified  $\text{Fe}_3\text{O}_4$  nanochains may have potential applications in biomedical area, including but not limited to artificial skin, artificial cartilage, tendon and clinical cancer treatment.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no financial and personal relationships with other people or organizations that can influence our work.

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