Preparation of wormlike PNIPAM microcontainers with magnetic nanoparticle inclusions

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1. Introduction

The unique properties of one-dimensional (1D) nanoparticle assemblies in electrics, optics, magnetism, and applications as sensors make them essential to the production of novel nanodevices as well as to the understanding of fundamental phenomena at nanometer scale [1]. Many methods have been developed to prepare 1D nanoparticle assemblies, including linear-template methods and template-free self-assembly methods. The self-assembly of magnetic nanoparticles into chains and flux-closure rings directed by magnetic dipolar interaction is an intriguing strategy [2,3]. It provides an alternative method for the bottom-up materials synthesis. By this method, nanostructures that are difficult for other methods to achieve can be prepared [4,5].

Poly(N-isopropylacrylamide) (PNIPAM) is one of the most widely studied environmentally responsive polymers owing to its thermosensitivity [6]. In aqueous solution, PNIPAM undergoes a phase transition from a hydrophilic state to a hydrophobic state as the temperature is raised above the lower critical solution temperature (LCST), which is about 32 °C [7]. PNIPAM nano- and microcontainers have attracted great interest due to their potential applications in drug carriers, confined reaction vessels, and protective shield for bioactive materials. In many applications, external control on materials is desired. For this reason, the preparation of PNIPAM microcontainers containing magnetic nanoparticles has received considerable interest. For example, Guo et al. [8] first prepared Fe3O4/SiO2/PNIPAM particles followed by selectively etching the silica template to gain PNIPAM microcapsules with magnetic cores. Chen et al. [9] prepared PNIPAM microcontainers containing Fe3O4 nanoparticles by a soft template method.

In this paper, we report the preparation of wormlike PNIPAM microcontainers with magnetic nanoparticle inclusions based on 1D self-assembly of magnetic nanoparticles and precipitation polymerization of NIPAM and N,N-methylacryloxypropyltrimethoxysilane (MPS). PNIPAM shell was fabricated on the P(NIPAM-co-MPS)-modified wormlike iron oxide/SiO2 nanostructures by precipitation polymerization of NIPAM and N,N-methylacryloxypropyltrimethoxysilane (MPS) followed by selectively etching the silica template to gain PNIPAM microcontainers containing magnetic nanoparticles.

2. Experimental

2.1. Preparation of wormlike iron oxide/SiO2 nanostructures and surface-modification with P(NIPAM-co-MPS)

Wormlike iron oxide/SiO2 nanostructures were prepared based on the method previously reported by us [10].

The prepared wormlike iron oxide/SiO2 nanostructures were then modified with P(NIPAM-co-MPS). In a typical process, 2.0 g (1.77 × 10⁻² mol) of NIPAM and 0.2 mL (8.43 × 10⁻⁴ mol) of MPS were dissolved in 25 g of tetrahydrofuran (THF). The solution was stirred at 350 rpm and deoxygenated by nitrogen for 30 min. After the mixture was heated to 65 °C, 10 mg (6.10 × 10⁻⁵ mol) of P(NIPAM-co-MPS) was added slowly to the solution, and the final mixture was stirred at 100 °C for 1 h. The precipitate was collected by centrifugation and washed with THF several times. The modified iron oxide/SiO2/PNIPAM particles were dried in vacuum at 40 °C.

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azobisobutyronitrile was added to initiate the polymerization. The reaction was performed for 8 h. After the mixture was cooled, the prepared wormlike iron oxide/SiO$_2$ nanostructures were added and stirred for 12 h. The mixture was then heated to reflux for 3 h. The product was centrifuged and washed with ethanol and water several times.

2.2. Encapsulation of wormlike iron oxide/SiO$_2$ nanostructures with PNIPAM

P(NIPAM-co-MPS)-modified wormlike iron oxide/SiO$_2$ nanostructures (10 mg) were dispersed in 30 mL of aqueous solution containing 50 mg (4.42 × 10$^{-4}$ mol) of NIPAM and 5 mg (3.25 × 10$^{-3}$ mol) of N,N$'$_methylenebisacrylamide (MBA). The dispersion was stirred at 200 rpm and purged with nitrogen for 30 min. After the mixture was heated to 70°C, 2 mg (7.41 × 10$^{-6}$ mol) of potassium persulfate was added. The reaction was performed for 4 h. The product was collected by centrifugation and washed with water several times. For increasing the thickness of the PNIPAM shell, the encapsulation process can be repeated.

2.3. Preparation of wormlike magnetic PNIPAM microcontainers

The as-prepared wormlike iron oxide/SiO$_2$/PNIPAM nanostructures were dispersed in NaOH aqueous solution (20 mL, 0.2 mol/L) and the mixture was stirred for 2 h. Then, the product was purified by three cycles of centrifugation, decantation, and redispersion in water.

2.4. Characterization

Transmission electron microscopy (TEM) images were obtained using a Hitachi H-600 microscope. High-resolution transmission electron microscopy (HRTEM) images were taken on a JEOL-2010 microscope. Gel permeation chromatography (GPC) was performed on a Shimadzu LC-10ADvp GPC instrument with THF as the eluent. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna 550 spectrometer using KBr disks. Thermogravimetric analysis (TGA) was performed with a Pyris 1 thermogravimetric analyzer at a heating rate of 10°C/min in nitrogen flow.

3. Results and discussion

The preparation procedure for the wormlike magnetic PNIPAM microcontainers is illustrated in Scheme 1. First, wormlike iron oxide/SiO$_2$ nanostructures were prepared. Then, the wormlike iron oxide/SiO$_2$ nanostructures were modified with linear P(NIPAM-co-MPS) chains. Subsequently, the modified wormlike nanostructures were encapsulated by PNIPAM shell through precipitation polymerization of NIPAM and MBA. At last, wormlike PNIPAM microcontainers with magnetic inclusions were obtained by removing the middle silica layer with NaOH.

Wormlike iron oxide/SiO$_2$ nanostructures were prepared based on 1D self-assembly of weakly ferromagnetic nanoparticles combining sol-gel chemistry through the method previously reported by us [10]. Fig. 1 shows a representative HRTEM image of the prepared wormlike iron oxide/SiO$_2$ nanostructures. A high contrast is observed between the inner magnetic nanoparticles and the silica shell. The magnetic nanoparticles of about 70 nm were regularly embedded in silica shell along the wormlike nanostructures. The thickness of the silica shell can be controlled by the added amount of tetraethyl orthosilicate (TEOS). As the amount of TEOS was 0.2 g, the thickness of the silica shell was about 45 nm.

![Fig. 1. HRTEM image of the wormlike iron oxide/SiO$_2$ nanostructures prepared with 0.2 g of TEOS.](image)

Scheme 1. Schematic illustration of the preparation procedure of wormlike magnetic PNIPAM microcontainers.
For fabricating PNIPAM shell on the wormlike iron oxide/SiO$_2$ nanostructures, the nanostructures were modified with linear P(NIPAM-co-MPS) chains. P(NIPAM-co-MPS) was prepared by solution polymerization of NIPAM and MPS in THF. The number average molecular weight ($M_n$) of the prepared P(NIPAM-co-MPS) (measured by GPC) is about $6.8 \times 10^3$ and the polydispersity index ($M_w/M_n$) is 2.76. The modification was directly carried out in the THF reaction medium. The linear P(NIPAM-co-MPS) chains contain $-\text{Si(OCH}_3)_3$ groups and can react with the silanol groups on the surface of the wormlike iron oxide/SiO$_2$ nanostructures. The successful modification was demonstrated by FTIR (Fig. 2A) and TGA (Fig. 2B). After modification, the characteristic peaks ascribed to amide I band (1653 cm$^{-1}$, C=O stretching) and amide II band (1559 cm$^{-1}$, N–H bending) appear, and the weight loss of the nanostructures at 600 $^\circ$C increases from 6.05% to 7.51%, indicating the successful modification of P(NIPAM-co-MPS) on the surface.

PNIPAM shell was fabricated on the P(NIPAM-co-MPS)-grafted wormlike iron oxide/SiO$_2$ nanostructures by precipitation polymerization of NIPAM and MBA. Fig. 3 shows the TEM images of the PNIPAM-coated wormlike iron oxide/SiO$_2$ nanostructures. By negative staining, the PNIPAM shell can be clearly observed. The thickness of the PNIPAM shell can be controlled by the coating times. Fig. 3A shows the TEM image of the wormlike iron oxide/SiO$_2$ nanostructures coated by PNIPAM once, the thickness of the PNIPAM shell is about 50 nm. If the nanostructures are coated twice, as shown in Fig. 3B, the thickness of the PNIPAM shell increases to about 120 nm.

The modification of P(NIPAM-co-MPS) plays a key role for the following fabrication of PNIPAM shell on the surface of the wormlike iron oxide/SiO$_2$ nanostructures. The comparative experiment showed that PNIPAM shell could not be formed on the bare nanostructures. In the past, for fabricating PNIPAM shell on silica particles, the surface was usually modified with silanes bearing reactive double bond, such as MPS [11–13]. The modification increases the hydrophobic character of the surface and promotes polymer attachment to the surface. In the beginning, we also tried using MPS-modified wormlike iron oxide/SiO$_2$ nanostructures as seeds to prepare core-shell nanostructures with a PNIPAM shell. However, no core-shell nanostructures were obtained and only pure PNIPAM microgels were generated. The reason might be due to the relatively large size of the wormlike iron oxide/SiO$_2$ nanostructures, which results in the deficit of surface area and depresses the efficient capture of reactive species at the beginning of the polymerization [11]. Therefore, it is supposed that the effect of P(NIPAM-co-MPS) modified on the wormlike iron oxide/SiO$_2$ nanostructures lies in two aspects. On one hand, P(NIPAM-co-MPS) chains collapse when the temperature is above the LCST and make the nanostructure surface hydrophobic. On the other hand, the collapsed long P(NIPAM-co-MPS) chains make the nanostructure surface rough, which results in the increase of the surface area and helps to the capture of reactive species during the polymerization.

The wormlike PNIPAM microcontainers with magnetic nanoparticle inclusions were obtained by removing the middle silica layer with NaOH. Fig. 4 shows the TEM image of the wormlike magnetic PNIPAM microcontainers. It is clearly observed that the silica layer has been removed. The microcontainers look something like magnetotactic bacteria [14]. Without the restriction of the silica layer, the magnetic nanoparticles can move freely in the microcontainers and the nanoparticle chains break. Under magnetic dipolar attraction, some magnetic nanoparticles assemble into short single chains. The wormlike magnetic microcontainers...
can be dispersed stably in water. When an external magnetic field is applied, the microcontainers can be readily separated from the dispersion due to the inner magnetic nanoparticles.

4. Conclusions

In conclusion, wormlike PNIPAM microcontainers with magnetic nanoparticle inclusions have been synthesized using wormlike iron oxide/SiO₂ nanostructures as template followed by removing the middle silica layer. The microcontainers simultaneously possess unique wormlike shape, thermosensitive shell as well as magnetic responsibility, which have potential applications in drug delivery system, protective shield for bioactive materials, etc.

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