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Organic-Dye-Coupled Magnetic Nanoparticles Encaged Inside Thermoresponsive PNIPAM Microcapsules

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We present a new approach for the fabrication of thermoresponsive polymer microcapsules with mobile magnetic cores that undergo a volume phase-transition upon changing the temperature and are collected under an external magnetic field. We have prepared organic/inorganic composite microspheres with a well-defined core–shell structure that are composed of a crosslinked poly(N-isopropylacrylamide) (PNIPAM) shell and silica cores dotted centrally by magnetite nanoparticles. Since the infiltration of template-decomposed products is dependent on the permeability of PNIPAM shells triggered by changes of exterior temperature, the silica layer sandwiched between the magnetic core and the PNIPAM shell was quantitatively removed to generate PNIPAM microcapsules with mobile magnetic cores by treatment with aqueous NaOH solution. For development of the desired multifunctional microcapsules, modification of the unetched silica surface interiors can be realized by treatment with a silane coupling agent containing functional groups that can easily bind to catalysts, enzymes, or labeling molecules. Herein, fluorescein isothiocyanate (FITC), which is a common organic dye, is attached to the insides of the mobile magnetic cores to give PNIPAM microcapsules with FITC-labeled magnetic cores. In this system, it can be expected that an extension of the functionalization of the cavity properties of smart polymer microcapsules is to immobilize other target molecules onto the mobile cores in order to introduce other desired functions in the hollow cage.

Keywords:
- core–shell materials
- fluorescence
- magnetic materials
- nanoparticles
- polymers

1. Introduction

Polymer capsules with shells made of environmentally sensitive materials[1] have attracted a lot of interest as a novel type of carrier or microreactor in recent years. Because they exhibit unique properties such as small size, large inner volume, and tunable permeability, they have wide applicability in submicro-to-micrometer encapsulation of drugs, enzymes, DNA, and other active macromolecules. However, especially in drug-delivery systems, many special requirements have to be fulfilled to complete the transfer and controlled release of objects at the right moment, in the right place, and at an adequate concentration guided by exterior stimuli including temperature, ion strength, pH, magnetic field and so on. Therefore, a considerable effort has been devoted to the development of multifunctional microcapsules. One of the more feasible routes is to incorporate functional nanoparticles into capsules with magnetic, fluorescent, and/or catalytic properties.

Up to now, magnetic nanoparticles have been utilized in biological applications such as magnetic resonance imaging (MRI) contrast agents,[2] tissue-specific releasing of therapeutic agents,[3] labeling and sorting of cells,[4] separation of

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 DOI: 10.1002/smll.200400145

biochemical products,[5] and drug-delivery systems.[6] Most of these applications require the nanoparticles to be chemically stable and well dispersed in a liquid medium. It has been demonstrated that an inert coating on the surface of magnetic nanoparticles could help prevent their aggregation in liquids and improve their chemical stability.[7] In recent years, due to the development of integrated multifunctional devices, magnetic nanoparticles have also been placed in smart polymer capsule systems as a component of the shell or as a part of the capsule interior. Among these microcapsules, hollow polyelectrolyte capsules are one of the most versatile systems. They are made by layer-by-layer (LbL) adsorption of oppositely charged polyelectrolytes on the surface of colloidal template particles, followed by removal of the templates.[8] Several other approaches have been reported in the past years. One such approach is to use hollow polyelectrolyte capsules as microreactors for spatially restricted inorganic synthesis.[9] The presence of polyelectrolytes such as poly(styrene sulfonate) and poly(allylamine hydrochloride) either inside or outside the capsule causes a pH gradient across the capsule shell.[10] The deposition of magnetic nanoparticles within the capsule interiors was carried out from the corresponding metal salts. A second approach is to use magnetic nanoparticles as one of the components of the polyelectrolyte shell by alternating adsorption with polyions and magnetic nanoparticles.[11] Magnetic capsules can be prepared by the sequential adsorption of magnetite nanoparticles and polyelectrolytes on PS templates, which can then be dissolved easily in THF. A third approach is to utilize the permeability of hollow polyelectrolyte capsules to allow infiltration of magnetic nanoparticles through homogeneously porous walls with a size scale of about 10 nm.[12] However, magnetic LbL capsules have some drawbacks compared to other applied capsules, such as poor reproducibility, time-consuming preparation, and low stability for small-sized capsules, which have some restrictions in their applications. At the same time, if the magnetic nanoparticles are adsorbed or fabricated on the shell of the polyelectrolyte capsules, the permeability of the shells will be influenced to some degree in the controlled-release process.

Poly(*N*-isopropylacrylamide) (PNIPAM) is a well-known thermoresponsive polymer[13] that exhibits a coil–globule transition in aqueous solution upon changing the exterior temperature. PNIPAM microgels have been applied in various biomedical fields, for instance as a supporting material for biological testing,[14] adsorption of proteins and active enzymes,[15] and temperature-triggered drug or chemical release.[16] Because PNIPAM microspheres can be utilized as a controlled-release system by changing the temperature, it can be expected that the molecules encaged in the hollow interiors will be controlled by the gated pores of the PNIPAM shells. In our previous work,[17] magnetite-doped silica spheres were prepared by a modified Stöber method. These inorganic composites could be used as a sacrificial template to prepare the core–shell hybrid particles.

In this paper, Fe_3O_4@SiO_2 microspheres were first coated with PNIPAM by precipitation polymerization, and then the silica template was selectively etched to form the target microcapsules. It is worth mentioning that the decomposition of the encapsulated templates is the key step for microcapsule fabrication. So far, little attention has been paid to utilizing the permeability of capsule shells to control the decomposition of template cores. In this paper, we have focused on the selective dissolution of templates to prepare thermoresponsive polymer microcapsules with magnetic nanoparticle cores. Since the shell pores of magnetic PNIPAM particles can be triggered from an open state to a closed state by a change of temperature, the silica layers sandwiched between the polymer shells and the magnetic cores may be controllably removed by changing the shell state. The capsule shells will keep the magnetic nanoparticles inside the microcapsules from aggregating by strong dipolar interactions or precipitating in poor solvents.

Another main motivation of this paper is the possibility to construct multifunctional capsules possessing several desirable properties in a single entity. Since the decomposition of the silica template is a controllable process, the fraction of silica residue on the mobile magnetic cores can be efficiently tuned, and the immobilization of fluorescence molecules that can be traced by fluorescence spectroscopy can be easily conducted. Fluorescein isothiocyanate (FITC), which is a popular fluorescence probe, has been chemically bonded to the mobile magnetic cores. The multifunctional microcapsules thus produced can provide the following desired functionality: 1) Due to the fast change of the thermoresponsive shells governed by the external temperature, the loaded molecules in the hollow cages can be controllably released; 2) the magnetite nanoparticles allow the manipulation of the microcapsules by an external magnetic field; 3) FITC molecules coupled on the magnetic cores allow the tracing of microcapsules by fluorescence spectroscopy in complicated systems. Owing to these advantages, these microcapsules could be used as a model to study the basic mechanism of chemical separation and purification, as controlled-delivery systems for drugs, and in other related biomedical fields.

2. Results and Discussion

2.1. Preparation of PNIPAM Microcapsules With Mobile Magnetic Cores

An iron oxide dispersion was prepared following the method described in reference [18], based on the co-precipitation of $FeCl_2$ and $FeCl_3$ upon addition of aqueous NaOH solution to a mixture of the iron salts. The obtained dispersion was treated with an excess of trisodium citrate solution to give stabilized magnetite nanoparticles. The modified Fe_3O_4 nanoparticles were easily coated by silica via the well-known Stöber process,[19] in which silica is formed in situ through the hydrolysis and condensation of tetraethyl orthosilicate (TEOS). The obtained Fe_3O_4@SiO_2 particle surfaces can be readily modified with commercially available silane coupling agents, such as 3-(trimethoxysilyl)-propyl methacrylate, and the PNIPAM shells with a cross-linker of *N*,*N*′-methylene bisacrylamide (MBA) formed by

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seed precipitation polymerization. In our previously prepared thermoresponsive polymer magnetic microspheres,[17b] the process of silica-coating the magnetite nanoparticles was carried out in a methanol/water mixture. In this case, we found it more difficult to coat the magnetic nanoparticles and adjust the shell thickness by changing several parameters. Such particles were therefore not fit for use as a sacrificial template to control the interior properties of the microcapsules. However, we found that the ethanol/water system was the most suitable. A typical recipe utilized a mixture of water (20 mL), ammonium hydroxide (2.5 mL, 25 wt.%), and a magnetite dispersion (1 g, 7 wt.%), which was poured into a mixture of ethanol (100 mL) and TEOS (2 mL) whilst stirring at 40 °C. After 12 h, monodisperse, 80-nm Fe_3O_4@SiO_2 particles had formed, as shown in Figure 1A. Note that the silica shell is homogeneous on each individual iron oxide particle, regardless of its original morphology. The well-defined core/shell nanoparticles become more monodispersed when the thickness of silica layers is increased.

Figure 1B shows the transmission electron microscope (TEM) image of the double-shelled, spherical particles of Fe_3O_4/SiO_2/PNIPAM containing 10 wt.% MBA (i.e., the weight percentage of MBA in the NIPAM monomers is 10%). The magnetite core (black dots in the center of the particles) of about 10 nm is encapsulated in a gray silica layer of about 40 nm, with a bright PNIPAM shell thickness of about 60 nm. In order to preserve the magnetite cores for obtaining PNIPAM microcapsules with a core/shell structure, the silica layer sandwiched between the magnetic core and the PNIPAM shell had to be selectively removed. Usually, hydrofluoric acid, a normal etchant of silica, is not suitable since it would remove the silica layer and the magnetic cores completely to yield completely hollow microcapsules. Therefore an aqueous NaOH solution was chosen to etch the silica layers. The image of Figure 1C shows that each hollow PNIPAM microcapsule contains one magnetic core, which sticks to the PNIPAM wall. It can be imagined that the magnetic cores are mobile inside the PNIPAM capsules in an aqueous medium (the hollow is filled with water). An AFM measurement demonstrated that, due to the loss of support of the interior silica layers, collapse at the top of the hollow spheres occurs, as observed in Figure 1D, and this explains well why the size of the microcapsules (Figure 1C) is much bigger than that of the solid ones (Figure 1B). Additionally, the mobile cores can stick to the walls, resulting in the protuberances on the surface of some etched microcapsules (see white arrow in Figure 1D). When the dispersion solution of PNIPAM microcapsules had dried on the glass matrix, the magnetic particles could be orderly arranged with the help of a magnet, as shown in the SEM image (Figure 1E). Rupture of the capsules was not observed. The reason for this may be that thick PNIPAM shells with 10 wt.% MBA are not easily destroyed since the hydrolysis of PNIPAM is slow at the low concentration of NaOH solution used.[20]

2.2. Selective and Quantitative Decomposition of Magnetite-Doped Silica Template

When the etching process was performed with a 0.1 M NaOH solution below the low critical soluble temperature (LCST) of PNIPAM, the PNIPAM particles were stable for some time, which allowed the fast decomposition of the silica templates; the weight loss of the silica layer reached about 82 wt.% immediately. Above the LCST of PNIPAM, deswelling of the PNIPAM walls may limit the erosion of silica by the alkali solution because the increased hydrophobicity of the PNIPAM walls prevents the diffusion of OH^- ions from the bulk medium across the shells of the microspheres. In this case, a controlled etching process could be conducted. Figure 2a shows the curve for controllable weight loss of silica layers in the microcapsules upon increasing the concentration of the aqueous NaOH solution

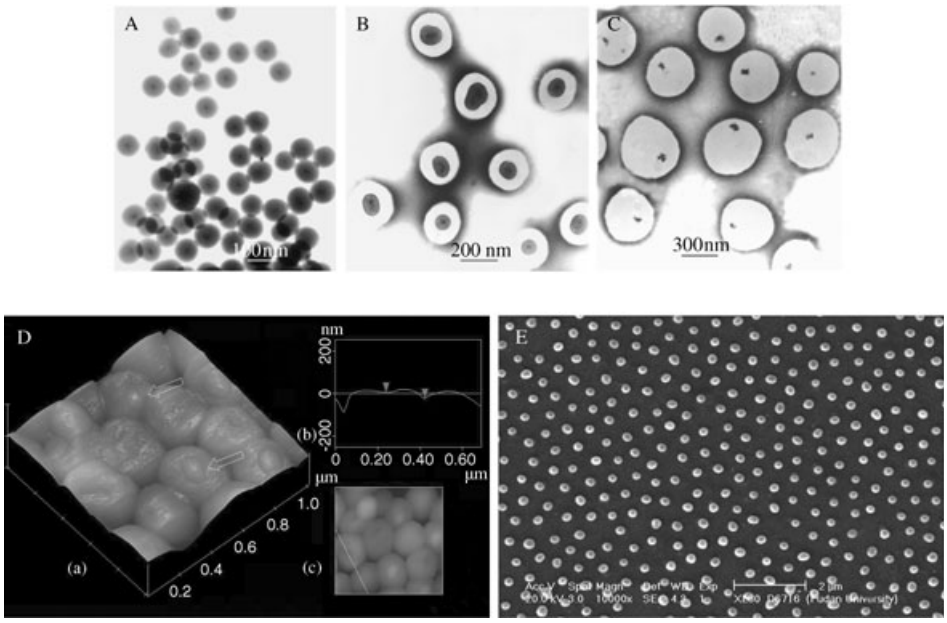

Figure 1. TEM images of Fe_3O_4@SiO_2 particles (A), Fe_3O_4/SiO_2/PNIPAM particles (B), and PNIPAM microcapsules with mobile cores etched by NaOH solution (C). D) AFM images of PNIPAM microcapsules with mobile cores, including a 3D image (a), a cross-sectional profile along the line in image c (b), and a 2D top-view image (1 μm × 1 μm) (c). E) SEM image of these magnetic capsules after positioning with a magnet during the sample drying process. The dark background of the TEM images (B, C) is obtained by staining with phosphate-tungstic acid.

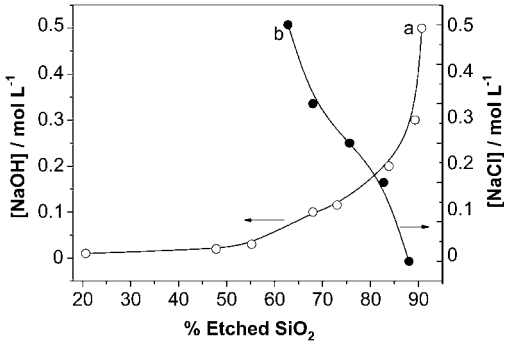

Figure 2. Effect of concentration of NaOH (a) and NaCl (b) solution on the alkali-etching process of magnetic PNIPAM particles as measured by TGA. Etching conditions: (a) changing NaOH concentration and adding NaCl solution to keep $[Na^+]=0.5$ M, at 50 °C; (b) changing NaCl solution concentration at [NaOH] = 0.1 M, at 50 °C. The precipitated particles were collected with a magnet and repeatedly washed to pH 7 by centrifugation.

and keeping $[Na^+]=0.5\ mol\,L^{-1}$ by adding NaCl solution at 50 °C. Owing to the shrinkage of the PNIPAM shell above the LCST, a poorer dissolution of particles is achieved at a fixed ionic strength above the LCST than below the LCST, which means that the decomposition of silica is more difficult. In these experiments, the high concentration of electrolytes used in our system may directly lead to the instability of the PNIPAM particles and then precipitation from the bulk medium in a short time at 50 °C. When a similar precipitation rate of particles was achieved by fixing the ion strength, a change of concentration of the NaOH solution gave interior cores with a different thickness of silica layer before the precipitates were collected with a magnet. Besides changing the alkali concentration, we also studied the role of the precipitation rate of microcapsules from aqueous solution on the etching process above the LCST of PNIPAM shells. The dependence of the weight loss of silica layers on the concentration of NaCl solution is plotted in Figure 2b. The experiment was conducted at [NaOH] = 0.1 M and 50 °C. As expected, an increase of the NaCl concentration leads to an increase of the precipitation rate of PNIPAM particles, which actually shortens the efficient etching time. When the NaOH concentration was fixed at 0.1 M, a different mass of silica layer was removed, as shown in Figure 2b, by varying the concentration of NaCl solution.

We chose three samples in Figure 2a to observe the inner shape of the microcapsules by TEM. The images in Figure 3 show these PNIPAM microcapsules with different thicknesses of the silica layer on the magnetic cores. From the TEM images, it can be seen that the decomposition of the SiO_2 template provides a hollow cavity in the capsules for potential applications, and it is also important that the residual SiO_2 on the mobile cores favors the of adsorption of target molecules and allows us to modify the interior environments of microcapsules.

The swelling/shrinking behavior of magnetic PNIPAM particles before and after alkali etching was measured by dynamic light scattering (DLS), as shown in Figure 4. All the volume phase transitions of the solid (Figure 4c) or hollow (Figure 4a, b) particles take place at about 32 °C and

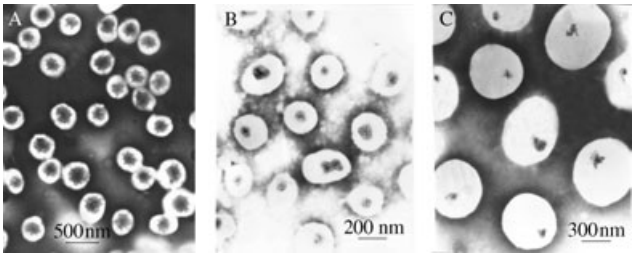

Figure 3. TEM images of alkali-etched PNIPAM microcapsules with mobile magnetic cores. The silica layer on the magnetic cores can be tuned by treatment with aqueous NaOH solution in a controllable etching process. The removed silica masses are 20.7, 55.3, and 83.9 wt.% for the particles shown in images A, B, and C, respectively.

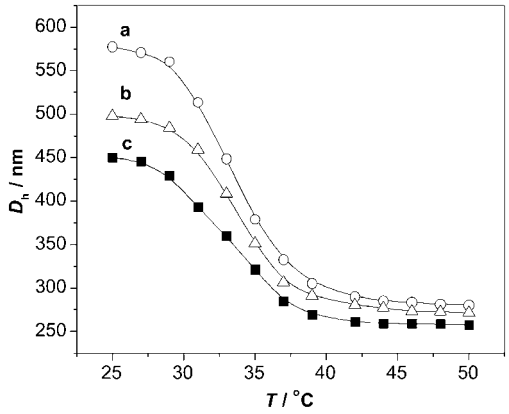

Figure 4. Hydrodynamic diameter of Fe_3O_4/PNIPAM microcapsules with 83.9 wt.% silica removal (etched by 0.2 M NaOH at 50 °C, keeping $[Na^+]=0.5$ M by adding NaCl solution) (a), Fe_3O_4/PNIPAM microcapsules with 55.3 wt.% silica removal (etched by 0.03 M NaOH at 50 °C, keeping $[Na^+]=0.5$ M by adding NaCl solution) (b), and Fe_3O_4/SiO_2/PNIPAM particles with 10 wt.% MBA (c), as a function of temperature.

their volumes clearly shrink upon increasing the temperature. As expected, the hollow particles have a bigger swelling ratio $(D_{25°C}/D_{50°C})^3$ than the corresponding solid ones. The swelling ratio changes from 5.3 to 8.7 for the Fe_3O_4/PNIPAM microcapsules with a silica weight-loss of 83.9 wt.% (a), and to 6.2 for microcapsules with a weight loss of 55.3 wt.% (b). Obviously, the interior composition may confine the swelling size of the PNIPAM solid particles below the LCST. Therefore, after the silica layers around the magnetic cores are removed by the NaOH solution, the PNIPAM walls can swell further without the limitation of the interior. The swelling-size of PNIPAM microcapsules that have lost 83.9 wt.% silica is bigger than that of 55.3 wt.% at 25 °C. Owing to the slight hydrolysis of the PNIPAM shells, the repulsion between the $-COO^-$ groups limits the shrinkage of PNIPAM shells at high temperatures. However, this small degree of hydrolysis does not result in the rupture of the microcapsules, and TEM, SEM, and AFM also demonstrated the integrity of the microcapsules.

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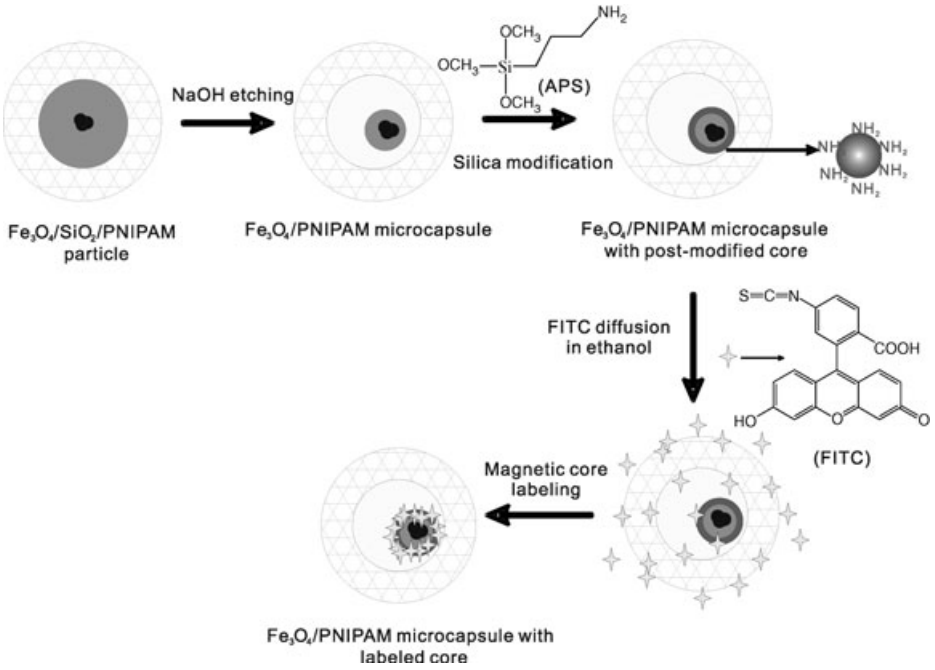
2.3. Modification of the Mobile Cores by FITC Molecules

For fabrication of microcapsules with an organic-dye-coupled magnetite core, special functional groups must be attached to the unetched silica layers by coupling agents. The target compounds with low molecular weight can then be loaded inside these microcapsules and subsequently change the interior physicochemical properties. We have demonstrated that encapsulation/release of FTIC molecules inside PNIPAM hollow spheres can be conducted by changing the external temperature.[21] Below the LCST of PNIPAM shells, the FTIC molecules penetrate the wall easily for labeling the mobile cores. Scheme 1 shows the main steps of this procedure. First, the thermoresponsive magnetic polymer particles based on crosslinked PNIPAM were prepared. Second, the silica layer sandwiched between the magnetic core and the PNIPAM shell was selectively removed by treatment with aqueous NaOH solution to generate PNIPAM microcapsules with a mobile magnetic core. In the next step, (3-aminopropyl)trimethoxysilane (APS) was used as a coupling agent and grafted onto the remaining silica layer of the magnetic cores. Finally, FITC was attached to the surface of the magnetic cores by the reaction between the amino group of APS and the isothiocyanate group of FITC,[22] resulting in PNIPAM microcapsules with mobile fluorescence-labeled magnetic cores.



Scheme 1. Schematic illustration of the fabrication of thermoresponsive PNIPAM microcapsules with mobile fluorescence-labeled magnetic cores. The stars represent the FITC molecules and the dark gray loop is a layer modified by APS.

PNIPAM microcapsules with 80.2 wt.% of silica layers removed were used for attaching FITC molecules onto the magnetic cores. These PNIPAM microcapsules can easily load APS molecules inside the hollow cage, and can be separated from the bulk solution with the help of a magnet. The hollow particles were dispersed in a mixture of isopropanol and deionized water, thus allowing the modification of the inner cores by APS on the silica surface of the microcapsules. Due to the maximum shrinkage of the PNIPAM capsules in this system,[23] the reaction was performed at pH 9 and a new silica layer was formed by APS. TEM studies showed that APS causes a slight increase in the core size. After FITC labeling, the temperature-induced dimensional change of the solid particles and microcapsules was measured by dynamic light scattering. The hollow particles have a bigger swelling ratio $(D_{25\,°C}/D_{50\,°C})^3$ than the corresponding solid ones, changing from 5.4 to 8.6. Interior chemical bonding does not affect the thermoresponsive properties of the PNIPAM shells. In addition, we showed that the FITC molecules are located in the hollow particles by marking with Cs^+ cations, which can stain the carboxylic groups (detected by TEM).[24] However, we were unable to show whether all the FITC is bonded to the mobile cores.

Figure 5 shows the fluorescence spectra of free FITC molecules, APS-FITC, magnetic PNIPAM microcapsules with labeled cores, and these capsules re-etched by NaOH solution. One single emission peak is observed for PNIPAM microcapsules with FITC-labeled cores (Figure 5c), similar to that

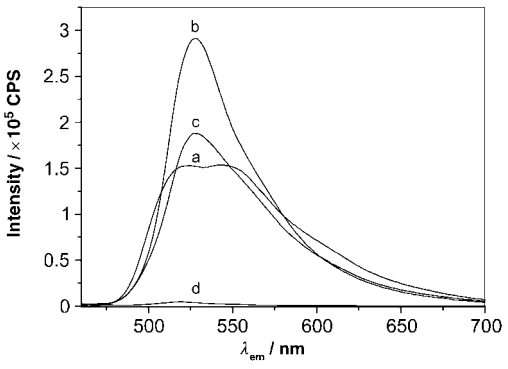


Figure 5. Fluorescence emission spectra ($\lambda_{ex} = 450$ nm) of free FITC (1.2×10^{-7} M) (a), APS-FITC (5.5×10^{-7} M) (b), fluorescent PNIPAM microcapsules (0.5 wt.%) (c), and PNIPAM microcapsules after re-etching (approx. 0.5 wt.%) (d). The measured samples were all dispersed in ethanol.

of APS-FITC (Figure 5b), which differ from the double peak of free FITC molecules (Figure 5a). This suggests that FITC molecules have reacted with the silica surface modified by APS in the microcapsule dispersion. After dialysis, the same fluorescence emission peak as that of ASP-FITC shows that the FITC molecules should be bonded to the mobile cores of the PNIPAM microcapsule. These PNIPAM microcapsules were treated with NaOH aqueous solution again and the fluorescence signal of the microcapsules disappeared completely after dialysis (Figure 5d), suggesting that the silica layer with FITC molecules had been removed. It was further verified that the FITC molecules were bonded to the mobile cores to give PNIPAM microcapsules with FITC-labeled mobile magnetic cores.

3. Conclusions

In summary, we have described the preparation of PNIPAM microcapsules with mobile magnetic cores. In a controllable etching process, the silica layers sandwiched between the PNIPAM shells and magnetic cores can be quantitatively removed to obtain PNIPAM microcapsules with mobile magnetic cores. FITC, a popular organic dye, was chemically coupled to the mobile cores inside the microcapsules. We envisage the use of the multifunctional microcapsules introduced in this paper for basic research in biomedical fields. These microcapsules undergo a reversible swelling–deswelling transition upon changing the external temperature, which could allow the loading of drugs, biomacromolecules, or chemical compounds and a temperature-induced release via the permeable PNIPAM shells. The encaged magnetite cores provide the possibility for manipulation of these carriers by collecting them at the appropriate sites with the help of an exterior magnetic field. The FITC molecules bonded to the cores can be traced easily by fluorescence spectroscopy, which helps to provide information about the distribution, enrichment, and transfer of microcapsules during the release process. Compared with other applied systems, these multifunctional smart microcapsules can be successfully prepared by a new approach that involves the quantitative and selective removal of silica templates and subsequent modification of their residue inside the microcapsules. This method realizes the combination of several desired functions in a single object.

4. Experimental Section

Synthesis of thermoresponsive magnetic particles: Colloidal magnetic nanoparticles were prepared by the chemical co-precipitation of Fe^{2+} and Fe^{3+} (molar ratio of 1:2) by treatment with an aqueous solution of sodium hydroxide.[18] The resulting solution was treated with nitric acid, followed by a trisodium citrate solution (0.3 M). The obtained iron oxide dispersion was stabilized in water and adjusted to 7.0 wt.% for further use. A suspension of the synthesized magnetic particles (1 g) was diluted with a mixture of ethanol (100 mL) and water (20 mL). After adding ammonia solution (2.5 mL, 25 wt.%), the tetraethylorthosilicate precursor (TEOS, 2 mL) was added to the reaction solution under continuous stirring at 40 °C for 12 h. The obtained silica-coated magnetite particles were modified with 3-(trimethylsilyl)propyl methacrylate (MPS) by stirring a mixture of silica dispersion and MPS (1 mL) for 12 h at 40 °C in ethanol. The resulting products were collected by magnetic separation and washed several times with ethanol and water. In the polymerization procedure, a 0.5 wt.% dispersion of the silica-coated magnetite particles grafted with MPS was used to seed the precipitation polymerization of *N*-isopropylacrylamide and *N*,*N*′-methylene bisacrylamide, using potassium sulfate (KPS) as an initiator. The reaction was allowed to proceed for 5 h at 70 °C. Finally, the core–shell particles were washed repeatedly with distilled water and enriched with the help of a magnet.

Preparation of magnetic polymer microcapsules: The polymer microcapsules were prepared by immersing the magnetic PNIPAM particles in NaOH aqueous solution at different temperatures for a given time. The resulting hollow microcapsules were collected by centrifugation and washed with deionized water until pH 7 was achieved.

Modification of magnetic cores trapped inside the PNIPAM microcapsules: To endow the magnetic cores with amino groups, (3-aminopropyl)trimethoxysilane (APS) was added, in excess, to a suspension of PNIPAM microcapsules with the mobile cores in isopropanol followed by ultrasonic dispersion for 30 min. Subsequently, the APS-loaded microcapsules were separated from the solution with a magnet and transferred into a mixture of isopropanol and H_2O (volume ratio of 1:1) maintained at pH 9 by addition of ammonia solution (25%) for hydrolysis and condensation between APS and the remaining silica layer. The modified microcapsules were washed repeatedly with ethanol and separated with the help of a magnet. FITC-bonded magnetic cores were obtained by the reaction between the amino groups of the APS-modified cores and the isothiocyanate groups of FITC (in excess) in ethanol for 12 h. Finally, the resulting products were collected with the help of a magnet and dialyzed to remove unreacted FITC.

Characterization: Transmission electron microscopy (TEM) images were obtained on a Hitachi H-600 transmission electron microscope, and the samples for TEM measurements were prepared by placing one drop of sample on copper grids coated with carbon, stained by phosphate-tungstic acid. Scanning electron microscopy (SEM) was carried out on a Philips XL30 microscope, and the samples were loaded onto a glass surface previously sputter-coated with a homogeneous gold layer for charge dissipation during the SEM imaging. The hydrodynamic diameter of the particles was determined by quasi-elastic light scattering (Malvern Autosizer 4700). Fluorescence spectra were measured on the undiluted stock dispersions with a FLS120 spectrofluorimeter. The samples were contained in a 1-cm quartz cuvette and illuminated with a Xe laser at a wavelength of 450 nm. Thermogravimetric analysis of the microcapsules with mobile magnetic cores was performed with a Pyrisis 1 TGA instrument at a heating rate of 10 °C min^{-1} in a nitrogen flow. Atomic force mi-

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croscopy (AFM) was performed with a Nanoscope IV. An aqueous dispersion of the samples was dropped onto a mica sheet and dried at room temperature.

Acknowledgement

We are grateful for financial support from the NSFC (No. 50173005, 50343019) and STCSM (03JC14012).

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Received: December 2, 2004
Published online on May 13, 2005

