Emulsion-Based Synthesis of Reversibly Swellable, Magnetic Nanoparticle-Embedded Polymer Microcapsules

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A one-step, template-free synthetic method for preparing polymeric microcapsules with iron oxide (γ-Fe_2O_3) magnetic nanoparticles (MPs) embedded in the polymer shell is reported. Using a simple emulsification of the multiphase mixture containing liquid prepolymer and MPs in chloroform solution, double emulsions comprising a chloroform core and MPs/polymer shell were spontaneously formed. After exposure to UV light, these double emulsions converted to microcapsules with a polymerized composite shell. The evolution from the double emulsions to the microcapsules was examined by confocal laser scanning microscopy. One unusual feature of these microcapsules is the ability to change shape reversibly by osmotic swelling of the water core upon repetitive drying and hydration. The microcapsules had an intrinsic superparamagnetic response due to the presence of the magnetic nanoparticles and could be moved and collected by external magnetic fields.

Introduction

Polymer microcapsules have attracted considerable attention recently due to their wide applications in drug delivery, food technology, catalysis, cosmetics, and as containers for confined chemical reactions.[1] Core−shell type microcapsules can be obtained by layer-by-layer (LbL) deposition of polyelectrolyte multilayers on a colloidal template, controlled phase separation, construction of colloidosomes, interfacial polymerization, coacervation, etc.[2−7] Composite microcapsules including an inorganic component are of particular interest, because incorporation of an inorganic material into the capsule structure could confer usable optical or magnetic properties as well as rigidity and structural stability. Various techniques for the fabrication of hybrid organic/inorganic capsules have been explored. Caruso et al.[8] reported the preparation of hybrid hollow spheres using layer-by-layer assembly onto a sacrificial colloidal template. The self-assembly of reactive block copolymers into vesicles could be used to make similar structures.[9] The simultaneous synthesis of an inorganic/organic material around microemulsion droplets represents another promising approach.[10] Several groups have demonstrated hollow polymeric spheres functionalized with metal and semiconductor nanoparticles embedded either in their core or the polymeric shell.[11] In particular, polymer capsules functionalized with magnetic nanoparticles (MPs) would be beneficial for many technological applications because MPs allow external manipulation of polymer capsules by a magnetic field. Among the various methods for imparting magnetic properties to polymer capsules, using layer-by-layer (LbL) polyelectrolyte multilayers assembly onto colloidal templates has been most

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widely pursued due to its synthetic versatility. In the LbL approach, MPs can be complexed with polymer capsules by (a) coating of MPs on a sacrificial colloidal template, (b) encapsulation of preformed MPs inside a capsule, and (c) synthesis of MPs on a capsule as a micro- or nanoreactor. The sacrificial template used in the method must be subsequently removed by chemical etching or calcination to get a hollow capsule structure.[12] The use of sacrificial templates, however, complicates the method and is not always compatible with drugs or other compounds that have to be encapsulated.

In this communication, we present a simple and straightforward method for producing polymeric microcapsules into whose walls iron oxide magnetic nanoparticles (MPs) are embedded. The microcapsule synthesis uses a one-step liquid−liquid dispersion technique broadly similar to the one developed by us earlier to synthesize polymer microrods.[13] A mixture of liquid prepolymer and MPs solution was emulsified inside a glycerin medium. The composition of the polymer solution and the presence of a surface active agent, however, lead to the immediate formation of stable double emulsions consisting of a liquid core/polymeric shell with embedded MPs. This double emulsion structure could be fixed by UV curing of the composite shell, evolving into a polymer capsule and embedding MPs in its shell. This method is very simple and scalable and does not need any kind of sacrificial template. Two features make the capsules synthesized of specific interest and significance. First, they are superparamagnetic and can be manipulated by external magnetic fields. Second, their liquid cores can be reversibly filled with water by osmotic swelling and drying.

Experimental Section

Materials. Iron (II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), 2-propanol (HPLC grade), concentrated ammonia, lauric acid (99.5%), chloroform, ethanol, rhodamine B, and glycerin were obtained from Aldrich. The UV curable liquid photopolymer NOA 61 was purchased from Norland Products (NJ). All chemicals were used as supplied without further purification.

Synthesis of Iron Oxide Magnetic Nanoparticles. Iron oxide (γ-Fe_2O_3, maghemite) magnetic nanoparticles (MPs) were synthesized using methods similar to that used by Moore et al.[14] A 0.5 g portion of $FeCl_3 \cdot 6H_2O$ was added to 50 mL of nitrogen-purged HPLC grade 2-propanol. Then, 0.25 g of $FeCl_2 \cdot 4H_2O$ was added while the solution was continuously stirred. The solution color was yellowish-orange after complete dissolution of the iron precursors. Then, the solution temperature was gradually raised to 50 °C and concentrated aqueous ammonia was added to the solution in excess, <10 mL. The color of the solution changed to dark brown after 15 min of continuous stirring. To speed up the precipitation of the MPs, the resulting solution was placed in a refrigerator for 5 h. The MPs were subsequently washed with methanol 3 times and settled by centrifugation at 10 000 rpm for 5 min. A 10 mM lauric acid solution, in 50 mL methanol, was then added to the MPs, and this mixture was stirred for 3 h. After completing the synthesis, the maghemite MPs were thoroughly washed with methanol to remove excess surfactant and finally dispersed in 50 mL chloroform. This MPs suspension was used as synthesized. The resulting lauric acid-stabilized maghemite MPs were single crystalline and uniform with diameters of ca. 5 nm (Figure 1).

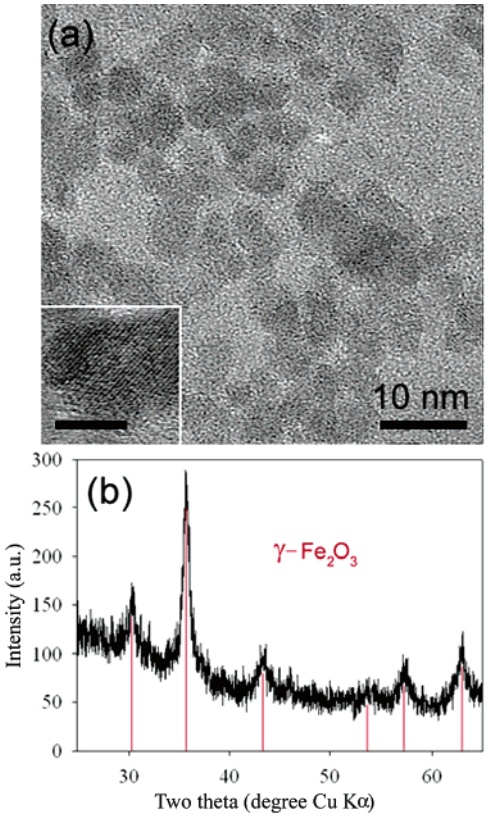

Figure 1. Characterization of the synthesized γ-Fe_2O_3 magnetic nanoparticles (MPs): (a) high-resolution TEM images (inset scale bar = 3 nm) and (b) XRD pattern. The nanoparticles have an average size of ca. 5 nm and single crystalline structure.

Synthesis of Polymer Microcapsules Embedded with MPs. During the microcapsule synthesis protocol, typically, 750 μL of a 1:2 (v/v) mixture (various volume ratios of the mixture 1:1−1:5 v/v were used) of the magnetic nanoparticle suspension (0.48 g/mL) and the NOA 61 prepolymer was evenly mixed by gentle shaking. Subsequently, the mixture was dispersed in 50 mL of glycerin by a Servodyne electronic mixer (Cole-Parmer, IL) at a rate of stirring 500 rpm for 10 min. The solution turbidity changed into a milky color after formation of NOA droplets containing magnetic nanoparticles. This dispersion was diluted with water (1:1 v/v) and placed in perfusion chamber (Cover-well, Grace Bio-Labs, OR) sealed with a microscope glass slide for UV curing. It was cured for 40 min by exposing it to a 100 W mercury lamp (365 nm, BL-100A UV lamp, Black-Ray, CA). After the polymer shells were fully cured, the capsules were collected by centrifugation, washed several times with deionized water, and redispersed in water.

Characterization. The capsules weres observed by optical microscopy (Olympus BX 61, equipped with high-resolution a DP70 digital charge coupled device (CCD) camera) with objective magnifications ranging from 4× to 50×. For field emission scanning electron microscopy (FE-SEM) (S-4700, Hitachi) and field

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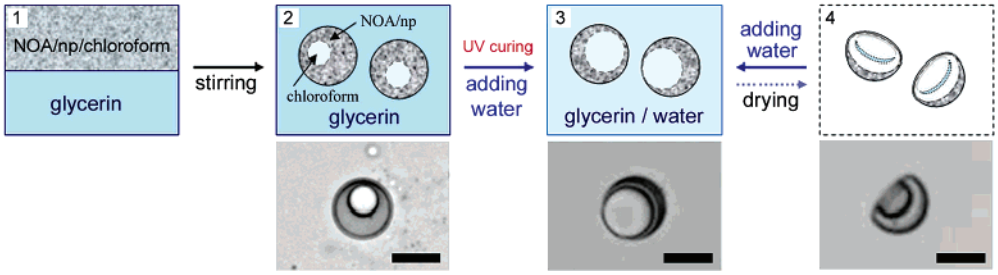

Figure 2. Schematics of the process for synthesis of the organic/inorganic hybrid microcapsules. The bottom frames are optical micrographs of the actual system (scale bar = 10 μm). (1) The mixture containing NOA prepolymer and iron oxide nanoparticles in chloroform is emulsified in the glycerin medium. After emulsification, double emulsions containing the chloroform core and nanoparticle containing polymeric shell are spontaneously formed. (2) After dilution of the glycerin medium with water, the inner chloroform core swells due to water permeation. (3 and 4) Curing and drying of the liquid medium results in organic/inorganic hybrid microcapsules, which reversibly swell in water.

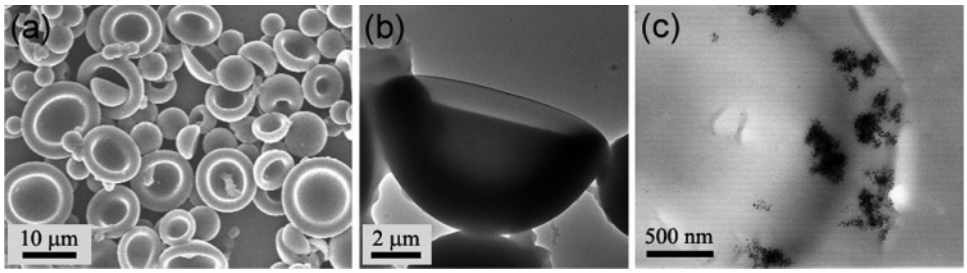

Figure 3. Microscopy images of the organic/inorganic hybrid microcapsules obtained by (a) SEM, (b) TEM, and (c) ultrathin (100 nm) cross-section TEM of the microtomed capsule. The sample is formed from a 750 μL mixture of the MPs/chloroform and NOA polymer (1:2 v/v), emulsified at a speed of 500 rpm (the average capsule diameter is 12 $\pm$ 3.28 μm).

emission transmission electron microscopy (FE-TEM) (TECNAI F20, Philips) analysis, a drop of sample solution was spread on a silicon wafer and carbon coated copper grid, respectively, and dried overnight at room temperature. The observations were carried out under accelerating voltages of 15 kV for SEM and 200 kV for TEM. A cross-section TEM image was taken from a sample of freeze-dried capsules dispersed in an epoxy matrix, cured at room temperature for 24 h, and microtomed. X-ray diffraction (XRD) of the magnetic nanoparticles was recorded using a Rigaku diffractometer equipped with a Cu Kα source. Confocal laser scanning microscopy (CLSM) images and intensity profiles were taken from a microcapsule sample from Rhodamine B dissolved in chloroform (5×10^{-3} mg/mL), with a Leica TCS NT confocal system (Leica Lasertec) equipped with a 100$\times$ oil immersion objective. Superconducting quantum interference device (SQUID) magnetic characterization of the microcapsules was performed on a Quantum Design (MPMS-XL) magnetometer.

Results and Discussion

The overall schematic for the organic/inorganic hybrid microcapsule synthesis is presented in Figure 2. The NOA prepolymer and maghemite magnetic nanoparticles (MPs) in the chloroform solution were mixed, after which the multiphase mixture was emulsified in a glycerin medium. Due to the high viscosity of the glycerin medium, kinetically stable emulsions can be formed without stabilizing surfactant. Quite unexpectedly, however, upon emulsification, this mixture spontaneously formed micron-sized double emulsions composed of a chloroform core and a polymer/MPs outer shell (Figure 2-2). These double emulsions could be converted into the hybrid microcapsules embedded with MPs, after polymerization of the composite shell by exposure to UV light (Figure 2-3 and 2-4). Electron micrographs of the hybrid microcapsules are shown in Figure 3. The images were taken from a sample comprised of a 750 μL mixture of the MPs/chloroform and the NOA polymer (1:2 v/v), which was emulsified at a speed of 500 rpm. Under these conditions, hybrid capsules with an average diameter of 12 $\pm$ 1 μm (standard deviation: 3.28 μm) were typically formed. Both SEM and TEM images of the formed hybrid microcapsules dried from water suspension showed a collapsed hemispherical capsule shell after drying and pointed out the existence of an inner hollow core (Figure 3a and b). A TEM image of an ultrathin cross section of the capsule is shown in Figure 2c. It was taken from a sample of freeze-dried capsules dispersed in an epoxy matrix, cured at room temperature for 24 h, and then microtomed. Due to the hydrophobic capping, the maghemite MPs were dispersed in the hydrophobic NOA polymer. Consequently, the MPs were captured into the solid NOA polymer phase, forming the composite shell of the microcapsules.

These hollow microcapsules were of size and morphology similar to the double emulsion droplets that had been spontaneously formed at the emulsification step. Thus, a composite shell of the MPs/polymer surrounding chloroform core structure was formed initially and was then converted to a microcapsule with a polymerized composite shell after exposure to UV light. It has been reported that polymer shell/liquid core capsules can be formed by the phase separation of polymer within droplets, as the polymerization proceeds.[3] In our case, however, a capsule structure with a liquid core is formed by phase separation even before the curing/polymerization stage. This was demonstrated by confocal laser scanning microscopy (CLSM) of the initial double emulsions. To visualize the formation of a chloroform core, we dissolved 5×10^{-3} mg/mL of Rhodamine B in the MPs/chloroform solution and, then, followed with the same emulsification procedure. Figure 4a shows an initial double emulsion structure with a MPs/NOA polymer shell and a

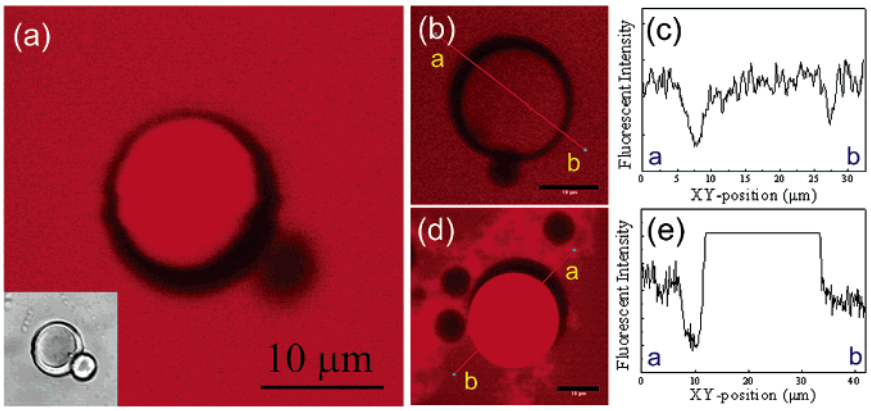

Figure 4. Confocal laser scanning microscope (CLSM) image of the double emulsions containing Rhodamine B dissolved in the chloroform core (a) before curing (inset: bright field mode) and (b) 10 min after formation (scale bar = 10 μm), (c) fluorescence intensity profile from part b along a line through the capsule center, (d) double emulsion after curing by exposure to UV light (scale bar = 10 μm), and (e) fluorescence intensity profile from part d along a line through the capsule center.

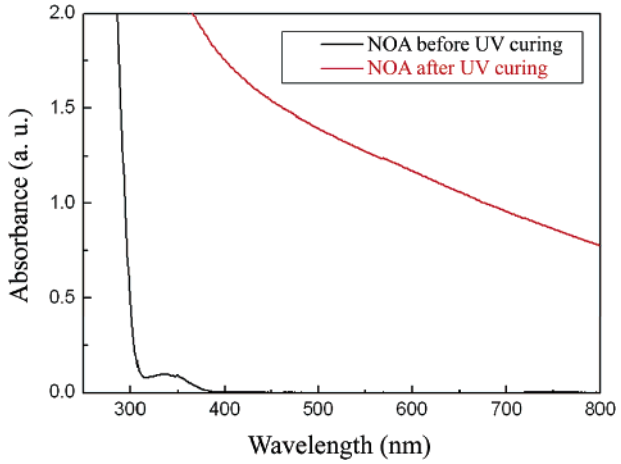

Figure 5. Spectral absorbance of polymerized vs nonpolymerized NOA. After curing, most of the microscope excitation light is filtered by the polymerized capsule shell; thus, the fluorescence quenching of the capsule interior is suppressed.

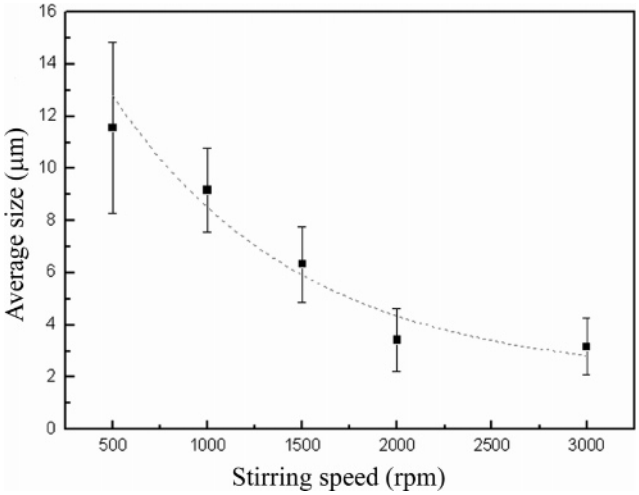

Figure 6. Relation between the average capsule size and the stirring (emulsification) speed. The droplet size decreases as the stirring rate increases.

chloroform core. Contrary to the dark region of the outer shell, the core has a very intense fluorescence, revealing the formation of a chloroform core inside the emulsion. We intentionally did not remove the residual dye from the glycerin medium, so the background fluorescence due to the diffusion of dyes during the stirring can also be seen. For double emulsion droplets, fluorescent intensity from the inner chloroform core and the background has been simultaneously quenched to a similar extent with time (Figure 4b and c). However, after UV curing (Figure 4d and e), the fluorescence from the capsule interior still remained intense, in contrast to the background fluorescence which is severely degraded by quenching. The fluorescence quenching of the capsule interior was hindered by the solidified polymeric outer shell which attenuates the intensity of the exciting beam (Figure 5).

The two critical factors ensuring high yield during the synthesis of hybrid microcapsules were the composition of the MPs/chloroform solution inside the emulsified mixture and the speed of emulsification. As shown in Figure 6, the speed of emulsification directly determines the average size of the capsules. The content of the MPs also can affect the overall capsule yield. For example, under an emulsification speed of 500 rpm, the highest yield (over 50%) of microcapsules was obtained when the content of the MPs/chloroform in the mixture was 20% (v/v). No capsules were formed in the absence of MPs. Speculating that the surfactant capping of the MPs surface plays a critical role in the capsule formation, we performed a comparative experiment using a small amount of a lauric acid surfactant without any MPs. Hollow capsule structures were also formed in this system when the content of the lauric acid in the NOA/chloroform mixture was within a range from 5×10^{-3} to 1×10^{-1} M.

We hypothesize on the basis of these observations that once the lauric acid-stabilized MPs are dispersed in the NOA prepolymer by the hydrophobic interaction, the lauric acid and the MPs change the balance of the interfacial energy of the polymer emulsion by preferential adsorption at the glycerin/NOA interface. The balance of interfacial energies becomes $\gamma_{C/G} > \gamma_{N/G} + \gamma_{N/C}$, where $\gamma_{C/G}$ denotes the interfacial tensions between chloroform/glycerin, and $\gamma_{N/G}$ and $\gamma_{N/C}$ correspond to the interfacial tensions of NOA/glycerin and NOA/chloroform, respectively. Thus, thanks to the lauric acid acting as a surface active agent, NOA spreads over the surface of chloroform, and the core/shell morphology is spontaneously formed within the emulsion droplet to minimize its surface free energy.[15] Quantitative studies on

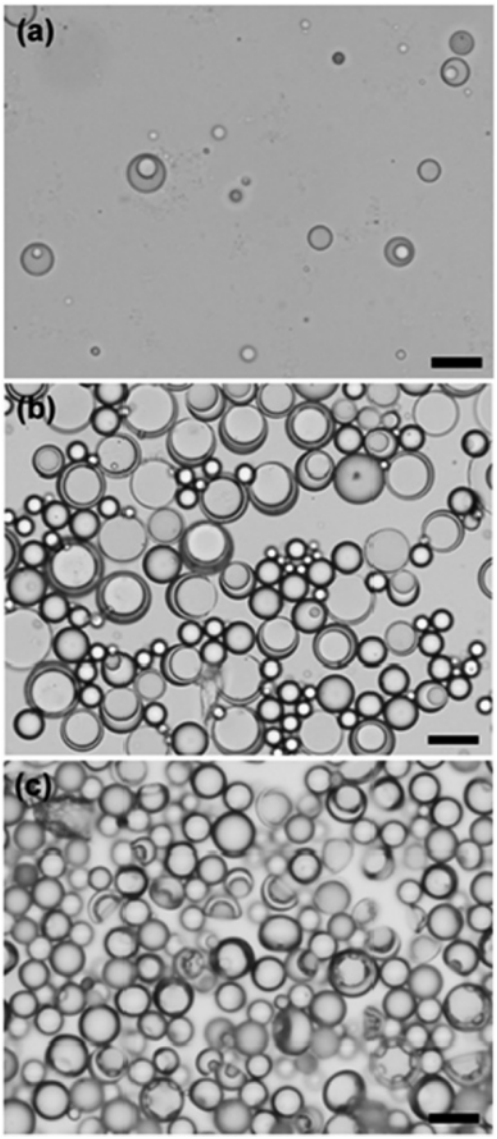

Figure 7. Micrographs of magnetic nanoparticle-embedded polymer microcapsules dispersed in (a) the pure glycerin medium and (b) pure DI water. (c) Micrograph of the capsules after drying. Scale bars are 20 μm.

interfacial energy change of the polymer emulsion in glycerin are currently in progress.

One interesting property of these hybrid microcapsules was their ability to reversibly exchange water with the environment (Figure 2). When the emulsions were exposed to water by dilution of the glycerin medium, their cores readily swelled due to the diffusion of water into the capsule interior (Figure 7). We believe that this core swelling is of osmotic origin due to the presence of a small amount of glycerin in the core. Moreover, when the shrunken dried capsules were redispersed in water after the chloroform in the core completely evaporated, they reswelled to their initial spherical shape. Up to seven drying/watering cycles were repeated, and the capsules showed fully reversible shape restoration. The permeation of water through the capsules was also confirmed by CLSM observations (Figure 8). The strong osmotic effect is also seen in observations of dye labeled

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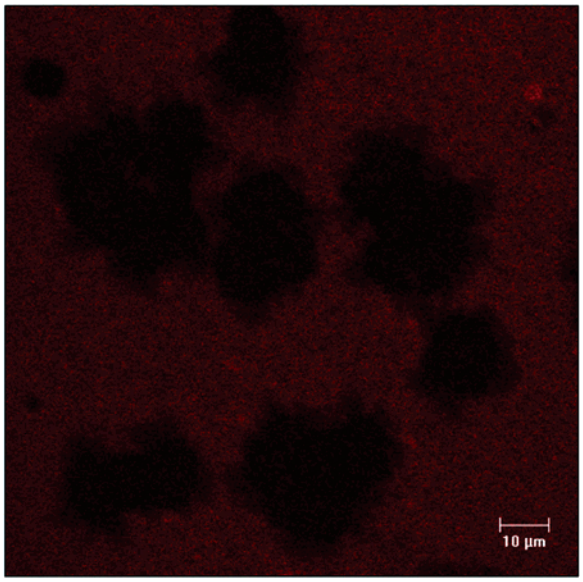
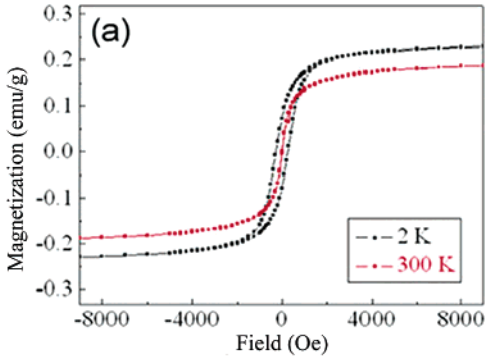


Figure 8. CLSM image of the exploded double emulsions, prepared with Rhodamine B dissolved in the chloroform/MPs/NOA mixture. When the initial double emulsions were exposed to water, they readily exploded due to the intensive incoming osmotic flux of water and lack of rigidity of the liquid walls.



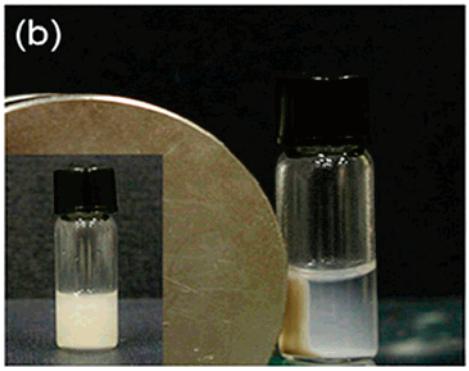


Figure 9. Magnetic properties of the hybrid capsules: (a) field-dependent magnetization curves and (b) capsule separation inside the container under an external magnetic field (inset: redispersed suspension).

double emulsions, where the cores readily exploded upon exposure to water, presumably by the high osmotic pressure of glycerin and water soluble dye in the capsule interior.

The nanoparticles embedded in the shells allowed easy manipulation of the capsules by magnetic fields. Magnetic hysteresis measurements at 2 and 300 K were performed using a superconducting quantum interference device (SQUID). As shown in Figure 9a, the capsules were superparamagnetic at 300 K and hysteretic at 2 K. Due to their small size

(ca. 5 nm) and single crystalline structure, the MPs embedded inside the capsules were superparamagnetic at room temperature.[16] As the capsule shell contained predominantly NOA polymer, the capsule exhibited relatively small magnetization. However, a clear magnetic response was evident and could readily be used to move and collect the capsules with an external magnetic field (Figure 9b).

A few aspects of this research could be of use in the development of new generations of microencapsulation techniques and products. The method reported here is very simple, straightforward, and, importantly, scalable. Few processes for one-step formation of multiple emulsions are reported in the literature, and the one-step formation of droplets with polymerizable outer shells reported here opens a range of new possibilities. The capsules formed in this process are of interest from two perspectives. First, they can be easily manipulated by magnetic fields, while being superparamagnetic, which would decrease clustering and aggregation, a common problem with many magnetic particles. The magnetic nanoparticles are enclosed within the polymer shell, which can minimize problems with leaching and unwanted chemical and biological interactions. The second unusual and potentially usable property of these capsules is the reversible swelling of the core in the presence of water thanks to the osmotic pressure of the residual glycerin on the inside. This process can enable, for example, biomedical application of these capsules. Most of the cores originally consist of chloroform, which can serve as a solvent for many drugs and other substances (that will be dissolved in the cores during the capsule formation process). To use these capsules in medical, pharmaceutical, and other products, however, the chloroform should be replaced with a benign liquid. This is exactly what our capsules allow by drying of the original chloroform cores and subsequent repeatable reswelling with water (see Figures 2 and 7). Once the capsules are refilled with water and delivered magnetically to the target area, the drug or other active component can diffuse slowly out. Thus, such capsules have a potentially rich range of biomedical and other applications, which is outside the scope of this report and will be a subject of our future studies.

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Conclusions

We report a new process for the synthesis of a polymeric microcapsule loaded with magnetic nanoparticles. The use of spontaneously formed double emulsions makes the method simple, facile, and scalable. The capsules demonstrated a unique water-sensitive morphology, as well as an inherent magnetic response from the presence of MPs. When filled with active ingredients, microcapsules of this type can find applications in drug delivery, as well as micro- and nanoreactors,[17] because the capsules can be filled with drug or reagent, swollen, and brought with a magnetic field to target area. The described strategy also could be used for the preparation of various types of microcapsules with interesting properties by changing the type of embedded inorganic nanoparticle and polymer used.

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