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Suspension polymerization based on inverse Pickering emulsion droplets for thermo-sensitive hybrid microcapsules with tunable supracolloidal structures

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ABSTRACT

Polymerization using Pickering emulsion droplets as reaction vessels is being developed to become a powerful tool for fabrication of hybrid polymer particles with supracolloidal structures. In this paper, two kinds of thermo-sensitive hybrid poly(N-isopropylacrylamide) (PNIPAm) microcapsules with supracolloidal structures were successfully prepared from suspension polymerization stabilized by SiO_2 nanoparticles based on inverse Pickering emulsion droplets. SiO_2 nanoparticles could self-assemble at liquid–liquid interfaces to form stable water-in-oil inverse Pickering emulsion. NIPAm monomers dissolving in suspended aqueous droplets were subsequently polymerized at different temperatures. The hollow microcapsules with SiO_2/PNIPAm nanocomposite shells were obtained when the reaction temperature was above the lower critical solution temperature (LCST) of PNIPAm. While the core–shell microcapsules with SiO_2 nanoparticles' shells and PNIPAm gel cores were produced when the polymerization was conducted at the temperature lower than LCST using UV light radiation. The supracolloidal structures with different cores could be tuned by simply changing reaction temperature, which was confirmed by confocal laser scanning microscopy and scanning electron microscopy. The interesting properties of both microcapsules were their ability of reversibly swelling during drying/wetting cycles and responsive to temperature stimulus. Such functional microcapsules may find applications in double control release system due to the presence of the supracolloidal structures and thermo-sensitivity.

1. Introduction

When solid particles instead of surfactant molecules are used to stabilize the emulsion, such emulsion is referred to as Pickering emulsion [1]. The solid particles are irreversibly located at the liquid–liquid interface and develop strong lateral interactions [2]. In the past few years, the Pickering emulsion droplets have been used as templates to prepare highly controlled elastic membranes and shells with the supracolloidal structures [3–14]. In the pioneer work, Velev et al. described the synthesis of hollow structures via templating oil-in-water emulsions stabilized by latex particles [8]. Later, Dinsmore et al. produced microcapsules, termed colloidosomes, by assembling the polymer latex colloid particles on the interface of the water-in-oil emulsion droplets, followed partial fusion of the polymer particles to obtain the elastic shell [7]. The colloidosomes offer great potential in controlling the permeability of entrapped species for the shell permeability can be controlled by adjustment of the partial fusion conditions. Different fabrication methods for colloidosomes have been reported including autohesion [7,9], chemical cross-linking of the solid particles [10], electrodeposition of polymers [11] and the gel trapping [12–14].

Most recently, Pickering emulsion droplets are used as polymerization vessels to fabricate hybrid polymer particles with supracolloidal structures [15–25]. The solid particles first self-assemble at the liquid–liquid interface and act as the effective stabilizers during the polymerization process without the need for any conventional stabilizers. After the polymerization completion, the particles are captured at the surface of the resultant polymer beads where they can be most effective for subsequent applications. Such surfactant-free emulsion polymerization, called Pickering emulsion polymerization is more attractive in the preparation of hybrid beads than the convention emulsion polymerization. Sometimes, this kind of polymerization is called as Pickering miniemulsion polymerization, suspension polymerization and dispersion polymerization. Howdle's group used Fe_3O_4 nanoparticles as a stabilizer for suspension polymerization of methyl methacrylate (MMA) in water and then successfully synthesized magnetic Fe_3O_4–PMMA nanocomposite polymer particles [15]. They also reported the preparation of hybrid polystyrene (PS) nanocomposite microparticles by an Fe_3O_4 stabilized dispersion

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polymerization [16]. Bon's group synthesized the clay-armored latex PS particles via Pickering emulsion polymerization and first systematically investigated the mechanism on Pickering miniemulsion polymerization using Laponite clay discs as stabilizers [17,18]. Voorn et al. prepared clay-armored polyacrylamide (PAAm) latex particles via inverse Pickering emulsion polymerization by using organically modified clay platelets as a stabilizer [19]. Jeng et al. fabricated composite latex particles prepared from Pickering emulsion polymerization of aniline/ZnO [20]. Polyaniline composites armed by different inorganic particles via Pickering emulsion polymerization have been also reported by He's group [21–23]. Zhao's group has used the surface-active nanoparticles with polymer brushes as emulsion stabilizers to prepare hybrid polymer colloid particles [24,25].

Polymerization based on Pickering emulsion droplets can also be used to fabricate inorganic/polymer hybrid hollow microcapsules. Bon's group used PMMA microgels to generate micron-sized Pickering emulsions as polymerization vessels to create supracolloidal interpenetrating polymer network reinforced microcapsules by phase separation [6]. The polymerized network should interlock the microgel building blocks and fix the core–shell morphology. At the same time the mechanical properties of the capsule can be readily tailored by varying the chemical composition of the interpenetrating polymer network. They also prepared organic–inorganic hybrid hollow spheres by TiO_2-stabilized Pickering emulsion polymerization [26].

Herein, thermo-sensitive hybrid poly(N-isopropylacrylamide) (PNIPAm) microcapsules with supracolloidal structures were prepared from SiO_2-stabilized suspension polymerization based on inverse Pickering emulsion droplets, as we inspired by the studies of Bon's group [26]. PNIPAm is temperature-responsive polymers having the lower critical solution temperature (LCST) around 32 °C. When the polymerization was carried out above the LCST of PNIPAm, the hybrid microcapsules with SiO_2/PNIPAm shell and liquid core were obtained. While below the LCST, the microcapsules with SiO_2 shell and uniform PNIPAm gel core were obtained. The thermo-sensitive microcapsules with aqueous cores or gel cores are ideally suited for biological encapsulation due to no contact with harsh solvents. The permeability of the obtained microcapsules could be double controlled due to the presence of the supracolloidal structures and thermo-sensitivity.

2. Experimental

2.1. Materials

Tetraethylorthosilicate (TEOS), ethanol, n-hexane, ammonium hydroxide (NH_3 25%) were obtained from Guanghua Chemical Factory Co. Ltd in China. N-isopropylacrylamide (NIPAm, KOHJIN Company) was purified by recrystallization from toluene. N,N′-methylenebisacrylamide (BIS, Acros), benzoyl peroxide (BPO, Shanghai Yunjie Company, China), 2,2-azobis(2-methylpropionamidine)dihydrochloride (V-50, Guangzhou Exhibition Biotechnology Company, China), fluorescein isothiocyanate (FITC, Alfa) were used as received. Water used in all experiments was purified by deionization and filtration with a Millipore purification apparatus to the resistivity higher than 18.0 MΩ cm.

2.2. Preparation of hydrophobic silica nanoparticles

Hydrophilic SiO_2 nanoparticles were fabricated according to the Stöber–Fink–Bohn method [27]. Water (4.2 ml), ethanol (22.2 ml), and ammonium hydroxide (NH_3 25%, 3.6 ml) were mixed together to form a solution. Tetraethylorthosilicate (TEOS, 8.1 ml) and ethanol (21 ml) were also mixed together. Then, two solutions were rapidly mixed and stirred for 12 h.

The hydrophilic SiO_2 nanoparticles were hydrophobically modified with dimethyldichlorosilane to attach silanol dimethylsilane ($SiOSi(CH_3)_2$)Cl groups on the surface and reduce the surface density of silanol groups [28]. Dimethyldichlorosilane (0.1 ml) was added into the silica dispersion (10 ml) containing silica nanoparticles (1 g) and the mixing suspension was stirred for 5 min at room temperature. After drying at 300 °C for 2 h, hydrophobic silica nanoparticles were obtained.

2.3. Preparation of PNIPAm/SiO_2 hybrid microcapsules

Hydrophobic SiO_2 nanoparticles (30 mg) were dispersed in 3 ml n-hexane by sonication. NIPAm (100 mg), BIS (10 mg) and V-50 (5 mg) were dissolved in 0.89 ml water. The aqueous solution was subsequently mixed with hexane including SiO_2 in a 10 ml bottle. A stable Pickering emulsion was obtained by hand shaking, and argon was bubbled through for 5 min. The suspension polymerization stabilized by SiO_2 nanoparticles was conducted at 60 °C for 8 h.

Pickering suspension polymerization was also carried out in an ice-water bath under 30 mW/cm^2 UV radiation for 5 min because water-soluble V-50 acts as both a thermo- and photo-initiator. The polymerization bottle was 47 cm away from the UV lamp.

The oil-soluble initiator BPO was also used to initiate Pickering suspension polymerization instead of V-50. BPO was dissolved in hexane. Pickering emulsion was formed as above-mentioned. The reaction temperature was 60 °C.

The experimental recipes for polymerizations at different conditions are shown in Table 1.

After polymerization, the hybrid microcapsules were on the bottom of the reaction bottle. Most of hexane was decanted and the prepared microcapsules were easily transferred into water.

Hybrid microcapsules were fluorescence labeled with FITC for confocal laser scanning microscopy (CLSM) testing. Acrylamide (Am, 10 mg) was copolymerized with NIPAm (100 mg) in Pickering suspension polymerization to prepare hybrid microcapsules. After polymerization, microcapsules were transferred into 10 ml $NaCO_3$–$NaHCO_3$ buffer (pH = 9.9). The fluorescent dye, FITC, was dissolved in DMSO at a concentration of 1 mg/ml. 100 μl of the dye solution were added to the buffer and oscillated for 24 h [29]. After reaction, hybrid microcapsules were washed with water until no free FITC was detected in the supernatant.

Table 1
Processing parameters for Pickering suspension polymerization.

Entry	Oil phase			Water phase				Polymerization		
	Hexane, ml	SiO_2, mg	BPO, mg	Water, ml	NIPAm, mg	BIS, mg	V-50, mg	Temperature, °C	Time, min	Conversion[b], %
HM-V0[a]	3	30	–	0.89	100	10	5	0	5	84.6
HM-V60	3	30	–	0.89	100	10	5	60	480	97.8
HM-B60	3	30	5	0.89	100	10	–	60	480	87.1

[a] Polymerization under UV radiation.
[b] Calculated from thermo-gravimetric analysis.

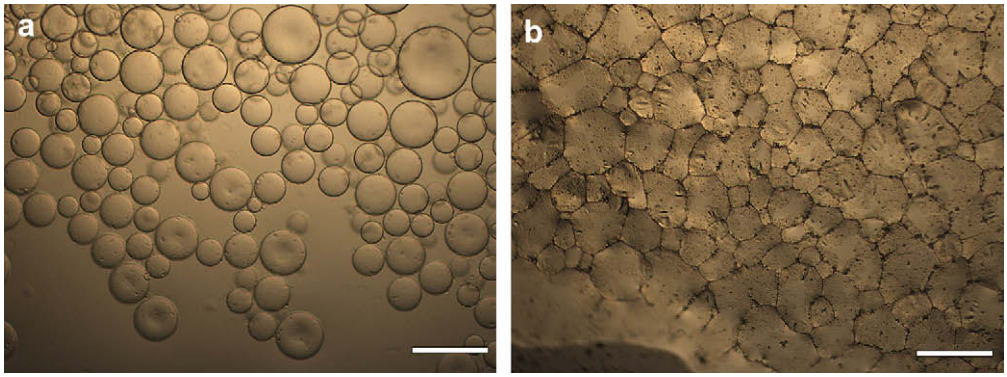


Fig. 1. Microscopical photos of the inverse Pickering emulsion before (a) and after (b) complete evaporation of hexane. Scale bar: 100 μm.

2.4. Thermo-sensitivity

The temperature response of PNIPAm/SiO_2 hybrid microcapsules was investigated using optical microscope with a hot stage. The variation of microcapsule size with temperature was measured by heating the samples on the hot stage and the heating rate was fixed at 1 °C/min.

2.5. Characterization

Zeta-potential of SiO_2 nanoparticles dispersed in pure water was determined with a Malvern Zetasizer Nano ZS90 and the zeta-potential value was the average of three measurements. The Pickering emulsion droplets and the hybrid microcapsules were observed with an optical microscope (Carl Zeiss, German) and the average diameter was estimated by counting 200 beads. More detailed structures were observed using a Philips XL 30 scanning electron microscopy (SEM) at the acceleration voltage of 15 kV. The air-dried or vacuum freezing dried samples were sputtered with gold. The confocal micrograph was taken with a Leica TCS-SP2 confocal laser scanning microscope (CLSM). The hybrid microcapsules were visualized by FITC-labeled copolymer at excitation wavelength of 485 nm. Thermo-gravimetric analysis (TGA) curves of the dry microcapsules were collected with a thermo-analyzer (TG 209, NETZCH Co.) within a temperature range of 20–800 °C and with the rate of increasing temperature of 10 °C/min.

3. Results and discussion

3.1. Formation of Pickering emulsions

For this work, silica particles were used as a stabilizer to form inverse Pickering emulsion. Firstly, hydrophilic SiO_2 nanoparticles of ca. 280 nm were prepared with zeta-potential of −56.7 mV. Secondly, hydrophilic SiO_2 nanoparticles were hydrophobically modified by reaction with dimethyldichlorosilane and zeta-potential decreased down to −2.3 mV. Finally, hydrophobic SiO_2 nanoparticles were introduced onto the liquid–liquid interfaces to produce water-in-hexane Pickering emulsion by shaking by hand because of the common sense that water-wet particles should stabilize o/w emulsions and oil-wet particles should stabilize w/o emulsions [2,30]. The resultant inverse Pickering emulsion is shown in Fig. 1a. The emulsion droplets were spherical from 10 μm to 100 μm with an average diameter of 70 μm. This emulsion was very stable and had no obvious change in 3 months. The dry emulsion droplets after complete evaporation of hexane are presented in Fig. 1b. Aqueous emulsion droplets were still independence and had a little distortion.

The number of silica nanoparticles N adsorbed on one droplet of water phase can be calculated from following Equation (1) [31]:

$$N = \frac{W_p}{\rho V_w} \times \left(\frac{D}{d}\right)^3 \quad (1)$$

where W_p is the weight of silica nanoparticles (0.03 g), ρ is the density of silica nanoparticles (2.07 g/cm^3), V_w is the volume of the water phase (1 ml), D is the diameter of the emulsion droplets (70 μm), and d is the diameter of silica nanoparticles (280 nm). Then the packing density f, that is, the surface area ratio for one Pickering emulsion droplet covered by silica nanoparticles, is given by Equation (2):

$$f = \frac{N\pi d^2}{4\pi D^2} = \frac{D}{4\rho d} \times \frac{W_p}{V_w} = \frac{70 \times 10^3}{4 \times 2.07 \times 280} \times \frac{0.03}{1} = 0.906 \quad (2)$$

According to Equation (2), the packing density f was 0.906 for the Pickering emulsion droplets in our experiments, which can be estimated that silica nanoparticles at the interfaces were basically monolayer. For comparison, a stable Pickering emulsion can also be generated by agitation using IKA Ultra Turrax T25 basic instrument at 11,600 rpm at 3 min. However, the average diameter of the droplets was similar with those prepared by shaking by hand.

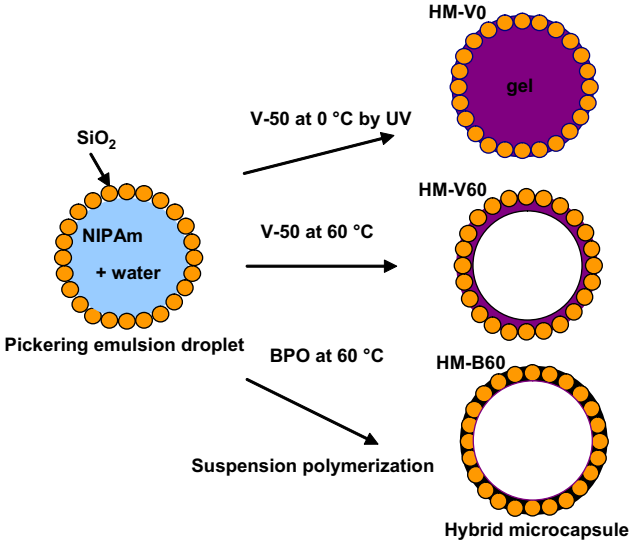


Fig. 2. Schematic illustration of the fabrication of hybrid microcapsules at different polymerization conditions.

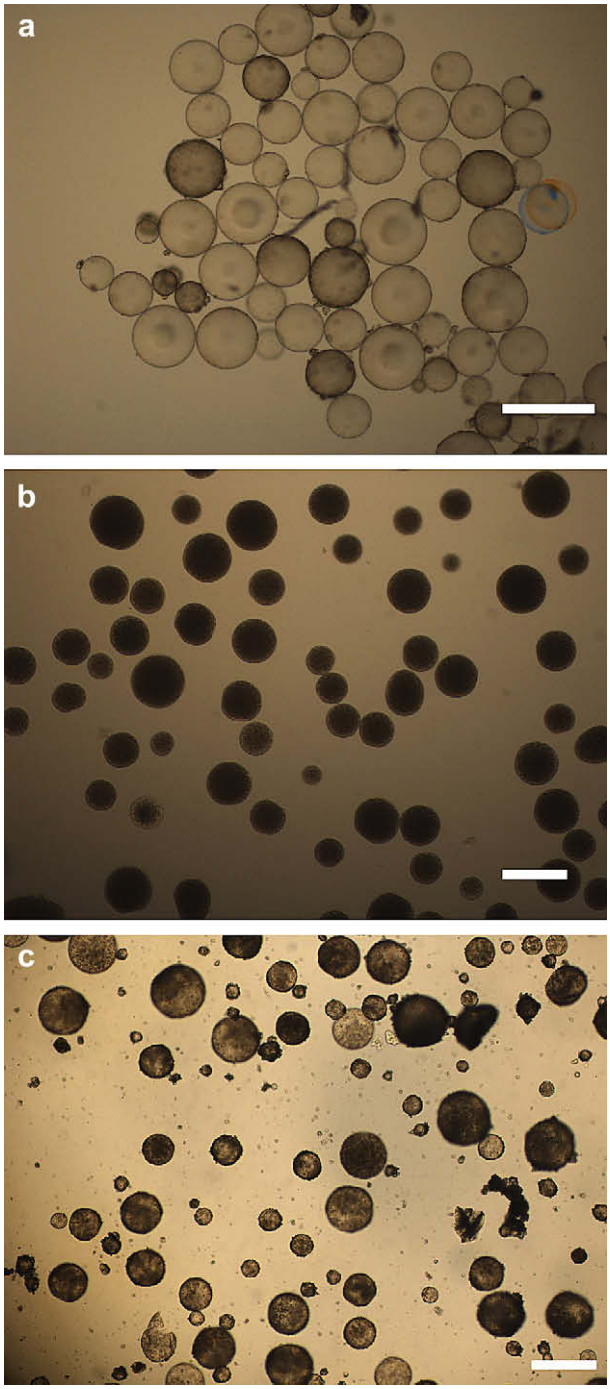


Fig. 3. Microscopical photos of the hybrid microcapsules transferred into water: (a) HM-V0, (b) HM-V60, (c) HM-B60. Scale bar: 100 μm.

3.2. Suspension polymerization based on Pickering emulsion droplets

After the stable inverse Pickering emulsion was produced, the aqueous emulsion droplets could be used as a polymerization vessel. For this suspension polymerization, the monomer NIPAm was dissolved in water before emulsification. SiO_2 nanoparticles act as an effective stabilizer during the polymerization and building blocks for creating supracolloidal structures after polymerization. According to the thermo-sensitive feature of PNIPAm, the hybrid microcapsules with different structures would be obtained by simply changing reaction temperature (above or below LCST of 32 °C). Two polymerization temperatures, 60 °C and 0 °C, and two initiators, water-soluble V-50 and oil-soluble BPO, were considered in our experiments. Three polymerization recipes are listed in Table 1. As shown in Fig. 2, when V-50 was used as the photo-initiator at 0 °C under UV radiation, the generated PNIPAm was hydrophilic in the polymerization process and randomly

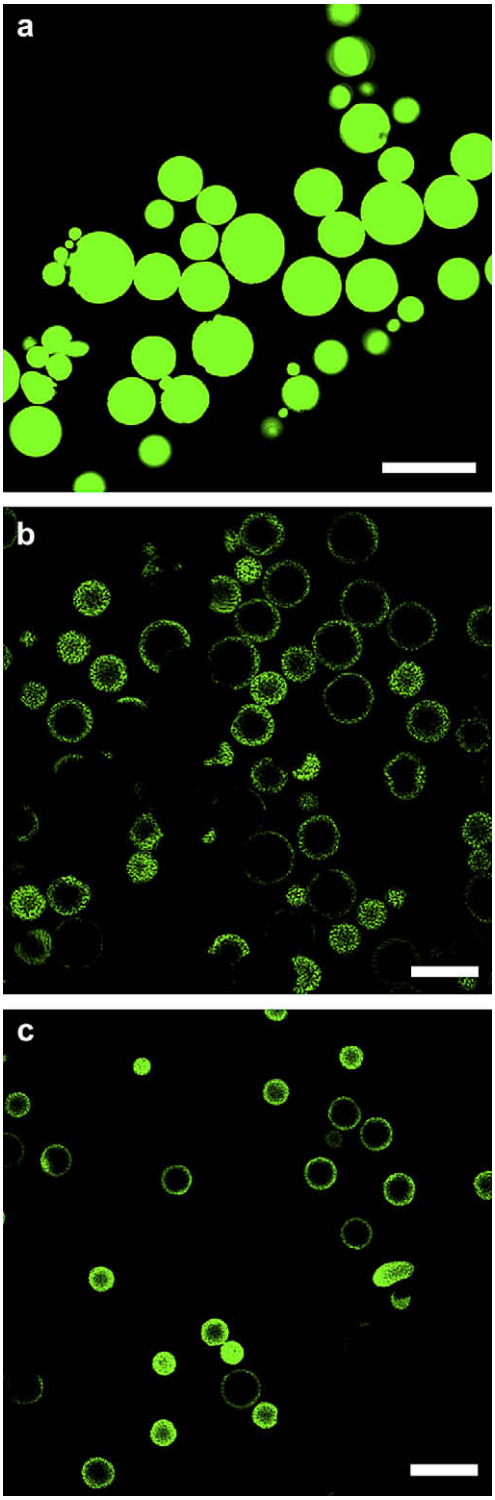


Fig. 4. Fluorescence images of the hybrid microcapsules: (a) HM-V0, (b) HM-V60, (c) HM-B60. Scale bar: 100 μm.

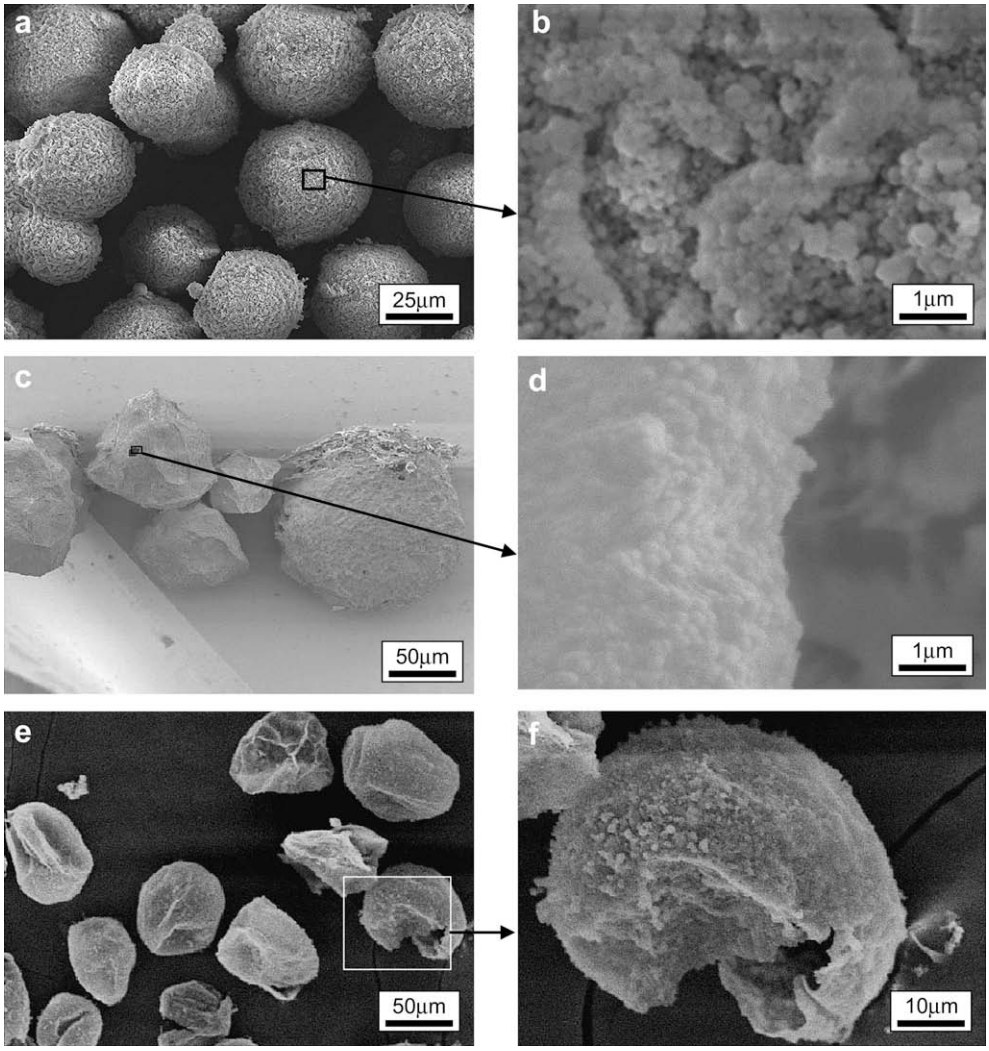


Fig. 5. SEM images of the hybrid microcapsules at different magnifications: (a,b) HM-V0, (c,d) HM-V60, (e,f) HM-B60.

distributed within the emulsion droplets. Finally the hybrid microcapsules with SiO_2 shells and uniform PNIPAm gel cores were obtained, which are referred to HM-V0. No leakage of inorganic particles is due to the support and trapping of gel cores [14]. While V-50 was used as the thermo-initiator at 60 °C, the generated PNIPAm which was hydrophobic in the polymerization process would gradually pile at the water/hexane interfaces to form nanoPNIPAm/SiO_2 aggregates. After the completion of the polymerization, the hollow microcapsules with nanocomposite PNIPAm/SiO_2 shells were obtained, which are referred to HM-V60. In contrast, the oil-soluble initiator BPO was used to polymerize NIPAm at 60 °C instead of V-50. The polymerization only occurred at the interfaces of the emulsion droplets. The interfacial polymerization also resulted in the hollow microcapsules with nanocomposite PNIPAm/SiO_2 shells. This kind of hybrid microcapsules is referred to HM-B60. Hexane was chosen as the oil phase for its easy evaporation (boiling point 69 °C) for Pickering suspension polymerization. Thus, washing for removing oil phase after polymerization was not required.

Typical microscopical photos of PNIPAm/SiO_2 hybrid microcapsules, HM-V0, HM-V60 and HM-B60 redispersed in water are presented in Fig. 3. Three kinds of the hybrid microcapsules were dispersed well in water and were from 10 μm to 100 μm with an average diameter of 70 μm like the original Pickering emulsion

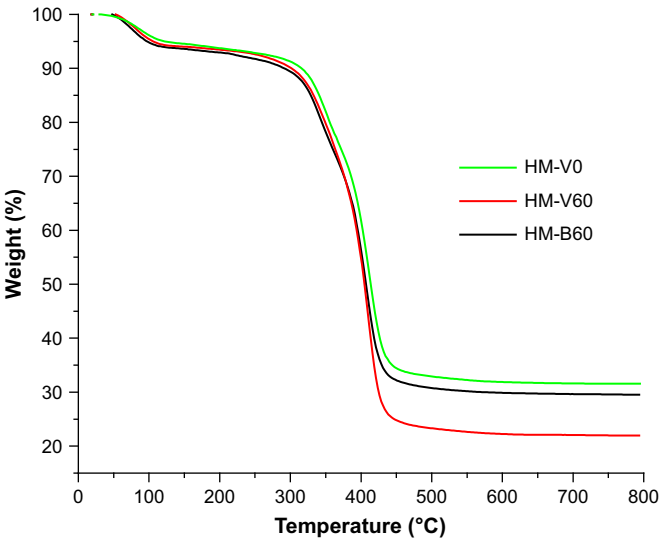


Fig. 6. TGA curves of the hybrid microcapsules.

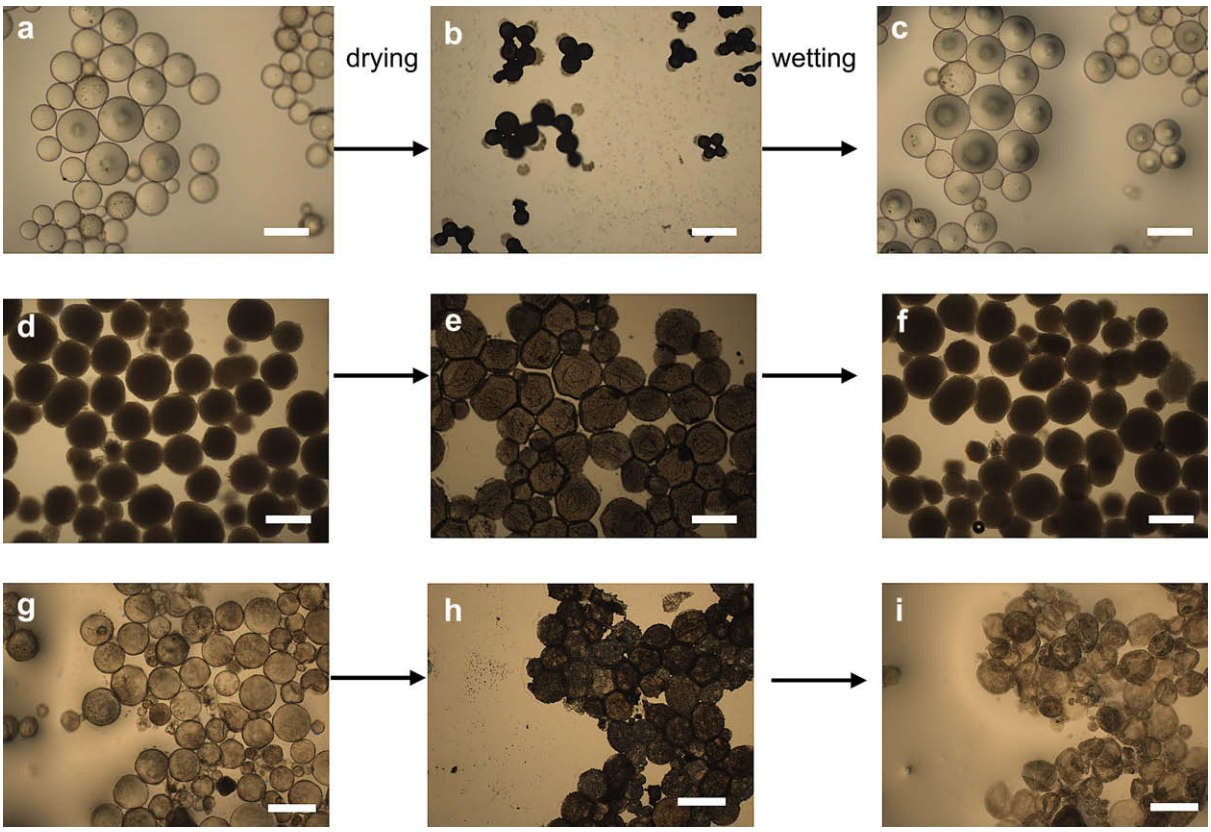


Fig. 7. Microscopical photos of the hybrid microcapsules during the drying/wetting cycle: (a–c) HM-V0, (d–f) HM-V60, (g–i) HM-B60. Scale bar: 100 μm.

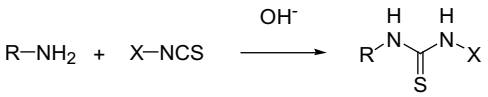
droplets, which demonstrates good stabilization of the SiO_2 nanoparticles during inverse emulsion polymerization. Mostly HM-V0 is transparent and spherical. HM-V60 is black and spherical by microscope observation and is white by naked-eye observation. However, HM-B60 is not as round as other microcapsules and the surface is rough. The fragments are observed in Fig. 3c. Polymerization initiated from the oil phase may influence the Pickering stabilization, so some Pickering emulsion droplets were destroyed and the irregular beads were obtained.

We also investigated the effect of the weight ratio of BIS:NIPAm to the hybrid microcapsules of HM-V60. When the weight ratio of BIS:NIPAm was from 0.12 to 0.05, HM-V60 was stable in the transferring process into water. When the weight ratio of BIS:NIPAm was less than 0.05, HM-V60 was unstable in the transferring process. In the other hand, we investigated the effect of the weight ratio of SiO_2:water to the hybrid microcapsules of HM-V60. With the increase of the weight ratio of SiO_2:water, the average diameter of HM-V60 decreased. The more detailed results will be investigated in the future work.

Suspension polymerization is a classic approach for preparation of polymer particles [32–34], while suspension polymerization based on Pickering emulsion opens a new way for preparation of a wide range of functional organic–inorganic nanocomposites.

3.3. Characterization

To observe the hybrid microcapsules by CLSM, acrylamide (Am) was introduced to copolymerize with NIPAm to add the amine group to the polymer matrices [35]. After the preparation of the microcapsules, the fluorescent dye, FITC, was reacted with the amine group in the polymer matrices to characterize the polymer distribution in the microcapsules. The reaction scheme for the copolymers with the fluorescence markers is as follows:



The fluorescence images of the microcapsules are shown in Fig. 4. From Fig. 4a, the uniform fluorescence intensity within HM-V0 was observed, which confirmed that a homogeneous polymer distribution was found throughout the whole microcapsules and the PNIPAm gel cores were formed. The fluorescence ring is observed in Fig. 4b for HM-V60 and Fig. 4c for HM-B60. It is obvious that HM-V60 and HM-B60 are hollow microcapsules with polymer shells and liquid cores.

More detailed structures of the hybrid microcapsules were observed by SEM as shown in Fig. 5. The sample of HM-V0 for SEM was prepared by the drying in air. The samples of HM-V60 and HM-B60 for SEM were prepared by the vacuum freeze-drying to keep the original spherical shape of the microcapsules. The diameter of dry HM-V0 was about a half of that of wet HM-V0 due to the shrinkage in the drying process (Fig. 5a). SiO_2 nanoparticles were found in the surfaces of HM-V0, indicating that they assembled at the water/hexane interfaces during polymerization and were used as building blocks for the fabrication of organic–inorganic hybrid materials (Fig. 5b). Combined with Fig. 4a, HM-V0 should be hybrid microcapsules with PNIPAm gel cores and SiO_2 nanoparticle shells. From the broken area of the shell in Fig. 5d, one can see that HM-V60 was hollow with PNIPAm/SiO_2 nanocomposite shells. From Fig. 5e and f, HM-B60 was hollow and the surface was rough. At polymerization at 60 °C, above LCST, water is non-solvent for PNIPAm and interfacial tension drives the polymer to separate towards the interface of the emulsion drop to form the polymer/inorganic shell and to obtain the hollow structure [36].

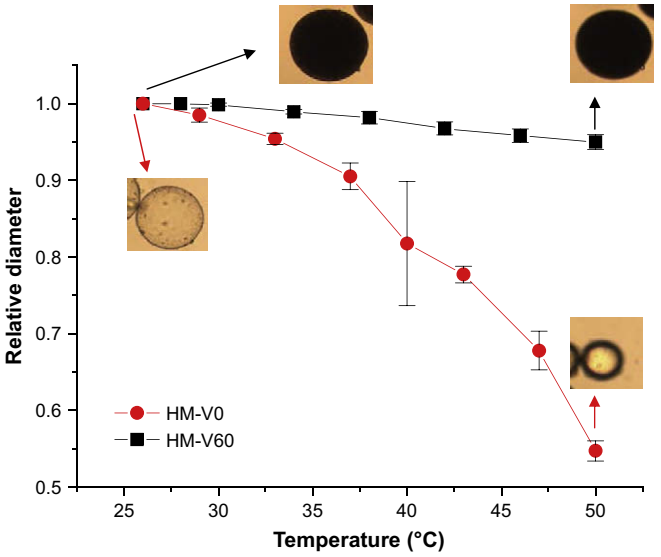


Fig. 8. Relative diameter of the hybrid microcapsules as a function of temperature. The inset pictures are microscopical photos of the hybrid microcapsules at different temperatures.

The dry hybrid microcapsules were analyzed by TGA to determine polymer and SiO_2 contents. The TGA curves are shown in Fig. 6. When temperature was raised to ca. 100 °C, weight loss of 6% was attributed to an elimination of remnant water from the microcapsules. Subsequently, there was a strong weight loss from ca. 300 °C to 450 °C due to the degradation of polymer chains. SiO_2 had not lost in the experimental temperature range. From Fig. 6, the PNIPAm weight contents in HM-V0, HM-V60 and HM-B60 were 66.5%, 76.9% and 68.5%, respectively. From the feed, the PNIPAm weight content should be 78.6% for all three samples. Then, the monomer conversion in the suspension polymerization was calculated to be 84.6% for HM-V0, 97.8% for HM-V60 and 87.1% for HM-B60.

3.4. De-swelling and swelling

One appealing property of hydrogel microcapsules is reversible de-swelling and swelling. The drying/wetting cycle of the hybrid microcapsules, HM-V0, HM-V60 and HM-B60 is presented in Fig. 7. Three microcapsules were dispersed well in ethanol (Fig. 7a,d,g). After the complete evaporation of ethanol, HM-V0 still kept spherical but the diameter had reduced to approximately 50% of the original (Fig. 7b). In contrast, dry HM-V60 and HM-B60 are flat like a round plate. When the dry microcapsules were redispersed in ethanol, HM-V0 and HM-V60 fully swelled to the initial spherical shape and no SiO_2 nanoparticles were out of the microcapsules during this process. This clearly demonstrates that the capturing upon the surface of microcapsules of SiO_2 nanoparticles is stable after the polymerization. The obtained hybrid microcapsules could be easily transferred to different external environments for the practical applications. However, when HM-B60 was redispersed in ethanol, the microcapsules could not restore perfectly to initial shape. The possible reason is that the PNIPAm/SiO_2 nanocomposite shells were unstable and HM-B60 got drawbacks easily in the de-swelling process.

3.5. Thermo-sensitivity

The thermo-sensitivity of the microcapsules HM-V0 and HM-V60 was also investigated. The thermo-sensitivity of HM-B60 was not studied because HM-B60 had a similar structure with HM-V60. Fig. 8 displays the average diameter change of HM-V0 and HM-V60 relative to that at 26 °C with temperature (T). With the increase of temperature, the microcapsules were shrinking. HM-V60 had a big size reduction of approximately 40% at T = 50 °C, while V50-H had a small size reduction of less than 6% at T = 50 °C. HM-V60 with a homogeneous PNIPAm gel core, could exhibit physical response to temperature like the PNIPAm microgel. The shrink of HM-V60 at high temperatures was restricted due to the location of PNIPAm only in the nanocomposite shell. With the increased temperature, the shell of the microcapsule should be more compact and the change of the diameter of the microcapsule may be not obvious. These two kinds of microcapsules with different temperature stimuli–responses may be applied in different 'on–off' regulations of drug release [37].

4. Conclusions

In summary, we have successfully prepared the PNIPAm/SiO_2 hybrid microcapsules via suspension polymerization based on inverse Pickering emulsion droplets. Silica nanoparticles self-assembled at liquid–liquid interfaces to form stable water-in-oil inverse Pickering emulsion and monomers dissolving in suspended aqueous droplets were subsequently polymerized. The hollow microcapsules with PNIPAm/SiO_2 nanocomposite shells and the core–shell microcapsules with SiO_2 shells and PNIPAm gel cores have been fabricated by simply changing reaction temperature. The hybrid microcapsules with aqueous cores could be easily transferred to water and be ideally suited for biological encapsulation due to no contact with harsh solvents. The hybrid microcapsules demonstrated their ability to reversible de-swelling and swelling during the drying/wetting cycle and thermo-sensitivity due to the presence of PNIPAm. These two types of microcapsules with different temperature stimuli–responses could be applied in different drug release models.

Acknowledgements

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