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Advanced Core-Shell Composite Nanoparticles Through Pickering Emulsion Polymerization

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1. Introduction

Solid particles have been identified as a new type of emulsifying agent in addition to surfactants and amphiphilic polymers since the pioneer studies by Ramsden in 1903 (Ramsden, 1903) and Pickering in 1907 (Pickering, 1907). Such emulsions are later on named as Pickering emulsions. In Pickering emulsions, solid particles of intermediate wettability in the size range from several nanometers to several micrometers attach to liquid-liquid interfaces and provide emulsion stability. Recently, there has been growing interest in Pickering emulsions because they open new avenues of emulsion stabilization and have numerous practical applications. For instance, we have studied the fundamentals of particle assembly in Pickering emulsions (Dai et al., 2005; Tarimala and Dai, 2004), utilized them as templates to investigate the dynamics of particles (Tarimala et al., 2004; Tarimala et al., 2006), and developed microrheology at liquid-liquid interfaces (Wu and Dai, 2006; Wu and Dai, 2007; Wu et al., 2009). In this chapter, we further apply the concept of Pickering emulsions to synthesize core-shell composite nanoparticles.

Organic-inorganic composites are vital in biological, medical, and chemical applications. Among them, core-shell composite nanoparticles are a unique class of materials which are attractive for wide applications. It is worthwhile to note that the composite nanoparticle structure in this study is opposite to the often reported core-shell structure in which inorganic particles serve as the core and polymer serves as the shell; here the polymer serves as the core and the inorganic particles serve as the shell. Such materials provide a new class of supramolecular building blocks and can “exhibit unusual, possibly unique, properties which cannot be obtained simply by co-mixing polymer and inorganic particles.” (Barthet et al., 1999) In comparison with the recently reported methods to synthesize core-shell composite particles, for example, post-surface-reaction (Ding et al., 2004; Lynch et al., 2005), electrostatic deposition (Dokoutchaev et al., 1999), and layer-by-layer self-assembly (Caruso, 2001; Caruso et al., 1999; Caruso et al., 2001), we synthesize core-shell composite nanoparticles through a novel Pickering emulsion polymerization route (Ma and Dai, 2009; Ma et al., 2010). Figure 1 illustrates the polymerization route and its comparison with the conventional emulsion polymerization.

Pickering emulsion polymerization is superior in several aspects: (1) no sophisticated instrumentation is needed; (2) a commercialized nanoparticle powder or solution can be

used without further treatment; (3) the synthesis can be completed in one-step; and (4) the produced particle dispersion is surfactant-free. Despite of these advantages, efforts to explore and utilize this approach are limited, although pioneer explorations have been initiated some approaches including miniemulsion polymerization (Bon and Colver, 2007; Cauvin et al., 2005), dispersion polymerization (Schmid et al., 2006; Schmid et al., 2007; Yang et al., 2008) inverse suspension polymerization (Duan et al., 2009; Gao et al., 2009), and inverse emulsion polymerization (Voorn et al., 2006) stabilized by fine solid particles.

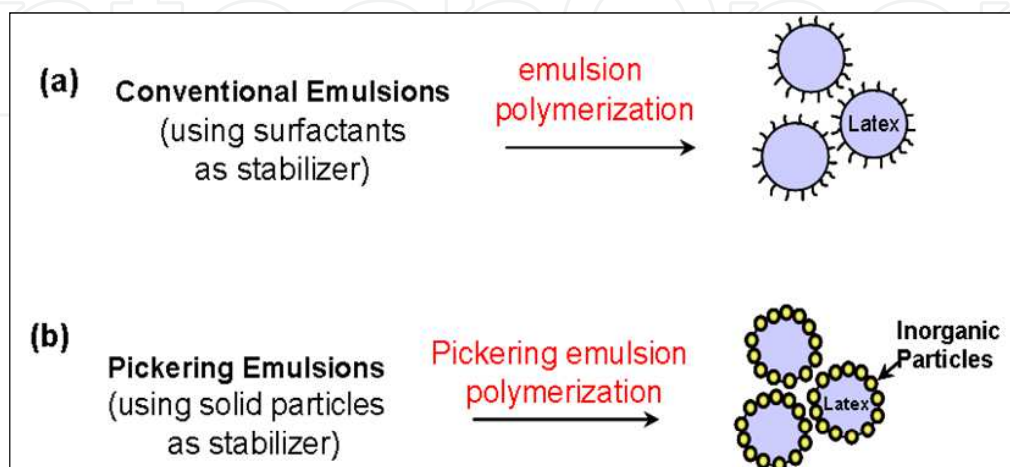


Fig. 1. Comparison between (a) conventional emulsion polymerization vs. (b) Pickering emulsion polymerization.

2. Pickering emulsion polymerization and its possible mechanisms

The general scope of Pickering emulsion polymerization is similar to that of emulsion polymerization, with the exception of using solid nanoparticles as emulsion stabilizers. Here we employ polystyrene (PS)-silica as a model system to illustrate its synthesis and explore possible mechanisms.

2.1 Synthesis and characterization of polystyrene-silica core-shell composite particles through Pickering emulsion polymerization

2.1.1 Materials and synthesis

IPA-ST silica solution, obtained from Nissan Chemicals, is 10–15 nm silica nanoparticles dispersed in 2-isopropanol. The silica concentration is 30–31% by weight. Nonionic azo initiator VA-086 (98%, 2,2-azobis(2-methyl-N-(2-hydroxyethyl)propionamide)), styrene monomer (99.9%), and HPLC grade water were purchased from Wako Chemicals, Fisher Scientific, and Acro Organics, respectively. All materials were used as received.

First, water, IPA-ST and styrene were agitated mechanically at 600 rpm for 8 min using Arrow 6000 (Arrow Engineering) in an ice bath to emulsify. Second, the emulsion was degassed with nitrogen and kept in nitrogen atmosphere under magnetic stir. When the temperature was raised to 70 °C, the initiator solution was added to start the polymerization. The composite particles were sampled at different time intervals ranging from 3 h to 24 h. Before characterization, samples were washed twice by centrifuging - redispersing cycles using an Eppendorf 5810R centrifuge. In each cycle, the sample was

centrifuged at 7000 rpm for 5 min, the supernatant was replaced with water and the sediment was redispersed by shaking manually.

2.1.2 Characterization of the polystyrene-silica core-shell composite particles

The synthesized polystyrene-silica core-shell composite particles through Pickering emulsion polymerization were characterized by various techniques. Figure 2(a) is a representative scanning electron microscope (SEM) image of the composite particles sampled at 5 hour reaction time. The roughness of the composite particle surfaces suggests that the particles are covered by silica nanoparticles. The core-shell structure can be clearly observed in the transmission electron microscope (TEM) image presented in Figure 2 (b). In many regions, the thickness of the shell is close to the size of one silica nanoparticle (10-15 nm), which may suggest a monolayer coverage. Furthermore, we employed hydrofluoric acid (HF) to dissolve the silica shell which led to the smooth PS core in Figure 2(c). The PS-silica compositparticle size and its distribution agree well with the dynamic light scattering (DLS) measurement, as shown in Figure 2(d). Finally, we performed energy dispersive x-ray (EDX) spectrum to confirm that a substantial amount of Si and O exist, as shown in Figure 2(e). Note that the relative intensity of the peak does not necessarily correspond to the true atom ratio in the sample. One of the main reasons is that the penetration depth of the electron beam is unknown. The penetration depth depends on various factors, such as the electron beam voltage, the nature of the sample, and the Au/Pd coating thickness during the sample preparation. The EDX result only provides qualitative information regarding the existence of silica, which composes of Si and O, in the composite particles.

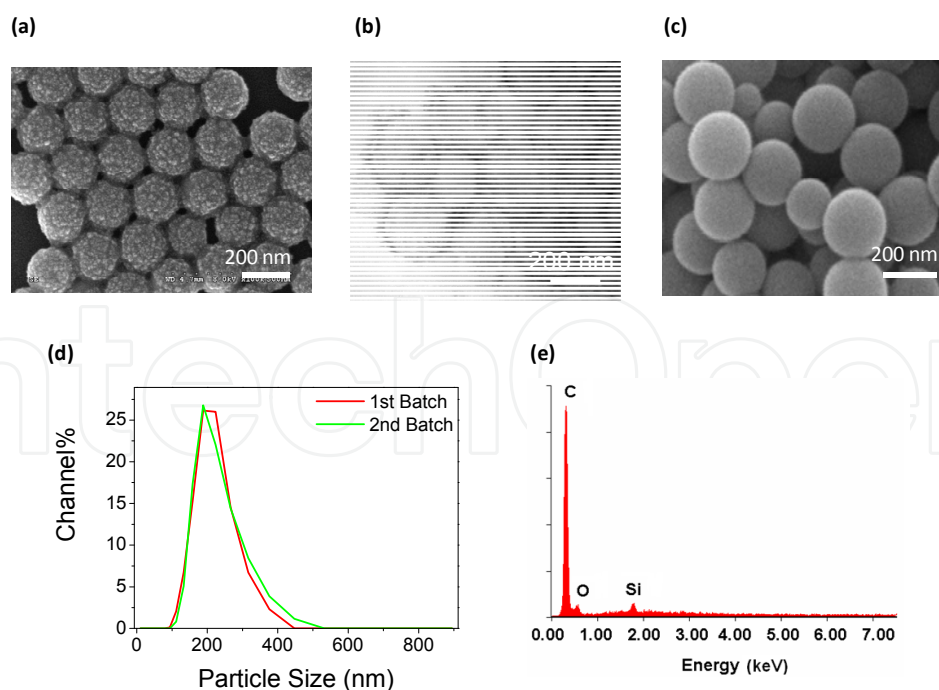


Fig. 2. Polystyrene-silica core-shell composite particles synthesized by Pickering emulsion polymerization: (a) a SEM image; (b) a TEM image of the cross-sectioned composite particles; (c) a SEM image of HF etched composite particles; (d) an overlay of DLS measurements of two batches; (e) an EDX spectrum.

It is worthwhile to note that we carefully selected VA-086 as the initiator. VA-086 is a water-soluble nonionic initiator and no success has been reported in surfactant-free emulsion polymerization of styrene (Tauer et al., 1999). In order to verify the sole stabilizing effect of silica nanoparticles, emulsifier-free emulsion polymerization using VA-086 as the initiator in the absence of nanoparticles was performed. No polystyrene particle formation was observed in the product, evidenced by SEM experiments. These experiments show that the initiator VA-086 has little effect on stabilizing the system in emulsion polymerization and therefore silica nanoparticles are the only source of stabilizer when present. In addition, VA-086 is neutral in charge thus is expected to minimize any electrostatic interactions with the negatively-charged silica nanoparticle surfaces which may complicate identifying silica nanoparticles as the sole stabilizer in emulsion polymerization.

The silica content is quantitatively determined by thermogravimetric analysis (TGA), as shown in Figure 3. Two samples were measured: the composite particles (solid line) and the composite particles after removal of the silica component by hydrofluoric acid etching, which is essentially polystyrene cores (dashed line). The polystyrene cores show a residual weight of approximately zero at 800 °C. Thus it is reasonable to assume that the major weight loss during heating is associated with the thermo-oxidative degradation of polystyrene and the residue close to 800 °C is solely silica. The silica content of the composite particles is approximately 20 wt%. Although some silica nanoparticles remain in the continuous phase and are washed off by centrifuging-redispersing cycles, the silica content of particles prepared via solid-stabilized emulsion polymerization using nonionic initiator VA-086 is significantly higher than that of particles (1.1 wt%) prepared via dispersion polymerization using nonionic initiator AIBN (Schmid et al., 2007). The improvement is likely due to the distinct polymerization mechanisms. In contrast to the dispersion polymerization in which the polystyrene monomers are dissolved in alcohols, the emulsion polymerization here contains distinguished liquid-liquid interfaces due to the immiscibility between the monomers and the aqueous continuous phase. Therefore the nanoparticles, even in the absence of electrostatic interactions, are thermodynamically favorable to self-assemble and remain at the liquid-liquid interfaces, following the same argument in Pickering emulsions (Dai et al., 2005; Tarimala and Dai, 2004). At the initial

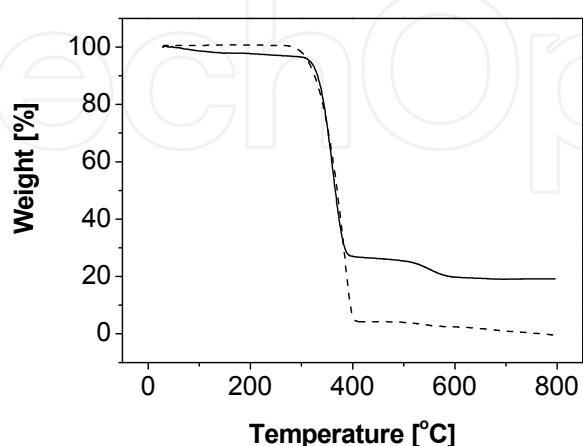


Fig. 3. Thermogravimetric analysis of the PS-silica core-shell composite particle prepared using VA-086 as the initiator before (solid line) and after (dashed line) HF etching treatment.

stage of polymerization, the nanoparticles provide stability to the monomer droplets. During the nucleation stage, silica nanoparticles are at the interfaces between the monomer phase and continuous phase. It is worthwhile to note that the role of silica nanoparticles described here is not the same as that in the polymerization involving oppositely charged initiator and nanoparticles (Schmid et al., 2007). In the latter case, the initiator molecules or residues adsorb onto the silica nanoparticle surfaces after initiation (Schmid et al., 2007) thus the silica nanoparticles function as the surface-active initiator residue. The mechanism of the core-shell structure formation in Pickering emulsion polymerization will be detailed later on.

2.2 Possible mechanisms of Pickering emulsion polymerization

The mechanism of conventional emulsion polymerization stabilized by surfactants has been under active discussion for over half a century and some consensus has been reached. Harkins proposed three loci of particle nucleation in 1947 (Harkins, 1947), which are later developed into at least three different nucleation mechanisms (Chern, 2006): the micellar nucleation, the homogeneous coagulative nucleation, and the droplet nucleation. Upon initiator addition and decomposition, free radicals form in the aqueous phase. The micellar nucleation (Chern, 2006; Tauer et al., 2008) begins with the capture of free radicals by micelles, proceeds with the continuous swelling and polymerization of monomers in the monomer-swollen particles, and finally terminates with the exhaustion of monomers. While some researchers believe that the micellar nucleation mechanism dominates at a surfactant concentration above the critical micelle concentration, doubts have also been raised (Tauer et al., 2008). In the absence of micelles, the homogeneous coagulative nucleation mechanism is likely dominant. In homogeneous coagulative nucleation (Chern, 2006; Feeney et al., 1984, 1987; Yamamoto et al., 2004), monomers dissolve in water and undergo radical polymerization to form oligomers. The oligomers coagulate to form embryos, nuclei, and primary particles sequentially. These primary particles, stabilized by the adsorption of surfactant molecules, could grow either *via* swelling of particles by monomers or deposition of oligomers onto their surfaces (Yamamoto et al., 2006). Finally, droplet nucleation is another possible mechanism in conventional emulsion polymerization. Here the monomer droplets may be subjected to the oligomeric radical entry and solidify into particles, following the droplet nucleation mechanism. Droplet nucleation is usually minor in emulsion polymerization, except in miniemulsion polymerization when hydrophobic initiators are used.

Based on the fundamental understandings in conventional emulsion polymerization, we propose possible Pickering emulsion polymerization mechanisms, taking into account the differences between fine solid particles and surfactant molecules. Since the nanoparticles do not form micelles like surfactant molecules, micellar nucleation is excluded. Thus, there are two possible nucleation mechanisms involved in the initial stage of Pickering emulsion polymerization. Homogeneous coagulative nucleation is likely to be the dominating mechanism here, which yields the sub-micron-sized particles. The droplet nucleation might also occur, which yields micron-sized particles. The two mechanisms are illustrated in Figure 4. Upon initiator addition, monomers dissolved in the aqueous phase react with decomposed initiators and form oligomers with radicals. In homogeneous coagulative nucleation, the oligomers coagulate into nuclei, which subsequently become monomer

swollen particles. Nanoparticles self-assemble at the interfaces between monomer and the continuous phase to provide stability. With the continuous supply of monomer molecules from the monomer droplets through diffusion, the particle size growth is mainly achieved by monomer swelling followed by polymerization within the core. In contrast, in droplet nucleation, initiated oligomers with radicals enter monomer droplets and subsequently polymerize into solid cores without significant size growth.

We use the hypothesized mechanisms to interpret the formation of polystyrene-silica nanocomposite particles prepared using VA-086 as the initiator. Figure 5 shows the dependence of particle size and surface coverage on reaction time and initiator concentration [Ma et al., 2010]. The composite particles are sampled from 3 h to 24 h reaction time and the initiator concentration relative to monomer is selected to be 0.83, 2.5, and 4.2 wt % respectively. At 3 h reaction time, well after the nucleation stage, composite particles with dense silica coverage are obtained. Since VA-086 initiator residues cannot provide sufficient stabilization to the monomer-swollen particles, silica nanoparticles would self-assemble at interfaces to provide stabilization and thus lead to high silica coverage. At initiator concentration 0.83 wt %, the silica coverage decreases with the particle size growth and the silica nanoparticles form patches on the nanocomposite particle surface with a low coverage. This might be an indication that the surface area of the polystyrene core increases with the particle growth without a significant increase of silica continuously attaching onto the polystyrene core. The particle growth mechanism is likely due to swelling of particles by monomers in the continuous phase. The same mechanism explains the surface coverage decrease in the system containing 2.5 wt % of initiator (images not shown) and from 3 h to 11 h in the system containing 4.2 wt % of initiator. These observations suggest that the Pickering emulsion polymerization using VA-086 as the initiator mainly follows the homogeneous coagulative nucleation mechanism.

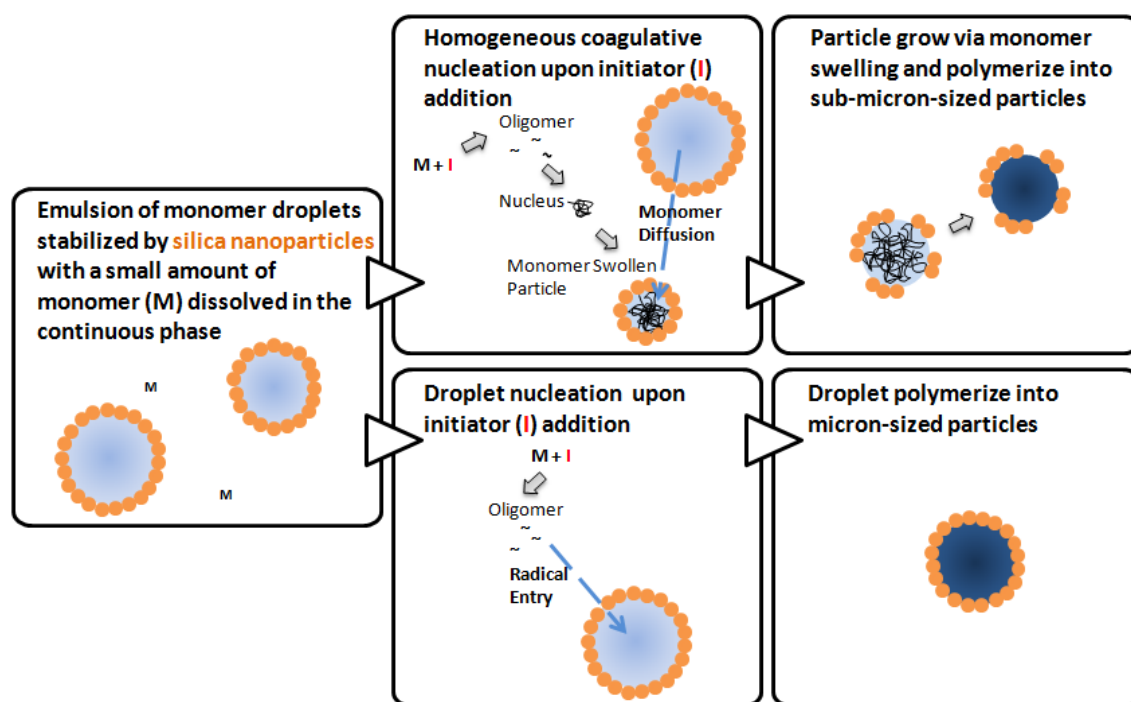


Fig. 4. Schematic illustration for possible mechanisms of Pickering emulsion polymerization.

One remaining mystery is the unexpected silica coverage from 11 h to 24 h in the system with 4.2 wt % initiator. Although the origin is unclear, we tentatively attribute the unusual silica coverage increase to the deposition of oligomers on the polystyrene core [Yamamoto et al., 2006], which adsorbed onto silica nanoparticles in the continuous phase [Yamamoto et al., 2006]. Excess initiator molecules might generate a large number of oligomers in the continuous phase, which could possibly adsorb onto silica nanoparticles. Thus when the oligomers on silica nanoparticles attach to preformed polystyrene surfaces, the silica nanoparticles are anchored there. It is also possible that the surface coverage increase might be due to the adsorption of depleted or close to depleted monomer droplets with a size below that of particles. It is worthwhile to note that the continuous phase contains approximately 21% isopropanol. The existence of isopropanol might increase the solubility of the monomer and the degree of polymerization required for an oligomer to be insoluble in the continuous phase, however, the solubility of monomer in the continuous phase is still low enough to enable emulsification and subsequent emulsion polymerization.

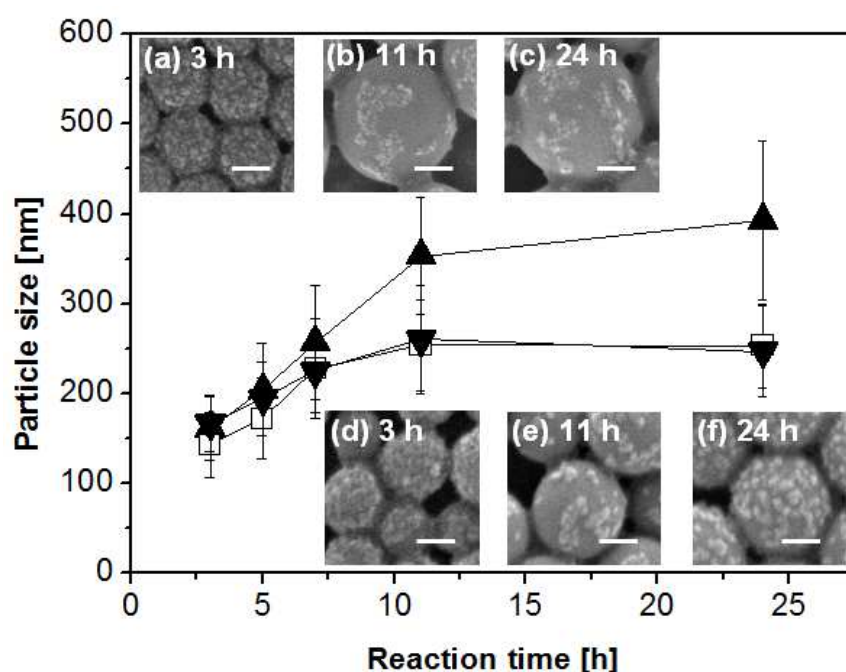


Fig. 5. Plot of particle size versus reaction time and representative SEM images with different initiator VA-086 concentrations: 0.83 wt % (▲, inset images a, b and c), 2.5 wt % (□) and 4.2 wt % (▼, inset images d, e and f). The error bars indicate the width of the particle size distribution and the scale bars represent 100 nm.

3. Environmentally responsive core-shell composite nanoparticles from Pickering emulsion polymerization

The Pickering emulsion polymerization opens a new and convenient way to synthesize core-shell composite nanoparticles. The simplicity enables further design and development advanced functional core-shell composite nanoparticles. One particular example to be illustrated here is the development of environmentally responsive core-shell composite nanoparticles from Pickering emulsion polymerization. By encapsulating drugs or chemicals, such nanoparticles enable controlled release upon environmental changes, as

shown in Figure 6. For example, other than the styrene monomer, we have incorporated NIPAAm (N-isopropylacrylamide) as co-monomer into the Pickering polymerization and synthesized temperature responsive PS/PNIPAAm-silica composite nanoparticles. PNIPAAm is a well-understood temperature sensitive gel, which undergoes volume shrinkage at a transition temperature of approximately 32 °C in pure water (Schild, 1992). The mechanism of this change is based on different solubility below and above the lower critical solution temperature (LCST) in aqueous media. Below the LCST, the polymer chain is hydrophilic as the hydrogen bonding between the hydrophilic groups and water molecules dominates; above the LCST, the polymer chain becomes hydrophobic due to the weakened hydrogen bonding at elevated temperature and the hydrophobic interactions among hydrophobic groups (Qiu and Park, 2001). Figure 7(a) is a representative SEM image of the composite particles sampled at 5-hour reaction time which shows that the particles tend to be spherical. The roughness of the composite nanoparticle surfaces suggests that the nanoparticles are covered by silica nanoparticles; this is contrasted by the smooth surface of the hydrofluoric acid (HF)-treated particles in Figure 7(b). HF dissolves the silica layer and leaves behind the smooth polymer surface. It is also evidenced by the blue line in the Fourier transform infrared (FTIR) spectrum in Figure 7(c) which shows that the composite nanoparticles have a characteristic strong peak at 1104 cm^{-1} , corresponding to the asymmetrical vibration of the Si-O-Si bond. Such a peak is absent in the red line in Figure 7(c) which represents the HF-treated composite particles. FTIR is a strong analytical tool which gives information about specific chemical bonds simply by interpreting the infrared absorption spectrum; here it is used to identify the presence of silica.

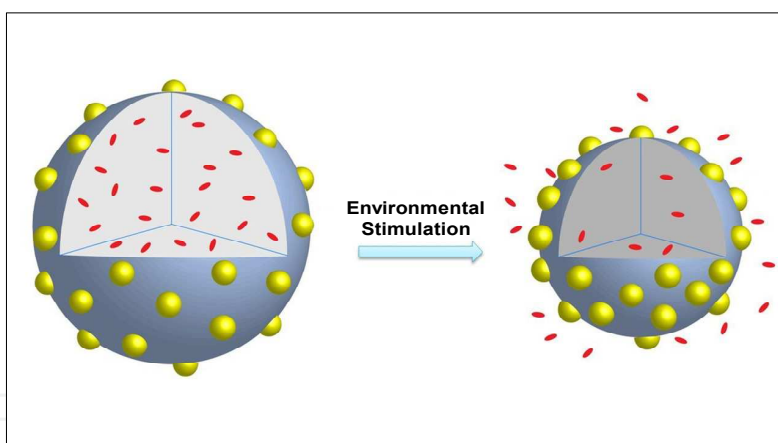


Fig. 6. Schematic illustration of environmentally responsive composite nanoparticles responding to an environmental change and releasing encapsulated materials such as a drug.

During our experiments, we also incorporated different ratios of monomer/comonomer in the formulation of the PS/PNIPAAm-silica core-shell composite nanoparticles. It is found that when the concentration of the NIPAAm monomer is high, the volume change of the nanoparticles is significantly greater with change in temperature, as shown in Figure 8. Control experiments of polystyrene-silica nanoparticles did not show a size transition over a temperature range of 25-45°C (data not shown). The transition temperature is not shifted by the silica nanoparticle encapsulation. This is consistent with the recently reported composite microspheres with a PNIPAAm core and a silica shell which also show a volume transition

starting at 32°C (Qiu and Park, 2001). It is likely due to the fact that silica particles are physically adsorbed on the surfaces of PNIPAAm microspheres thus no chemical bond formation with silica occurs which might change the transition temperature. Moreover, the copolymerization with styrene has no significant effect on the transition temperature. One hypothesis is the relative phase separation of PNIPAAm and polystyrene within the core. Duracher et al. studied PNIPAAm-polystyrene particles and suggested a PNIPAAm-rich shell and a polystyrene-rich core structure (Duracher et al., 1998). Such phase separation may also occur in the core of the composite particles here although detailed morphology is unknown.

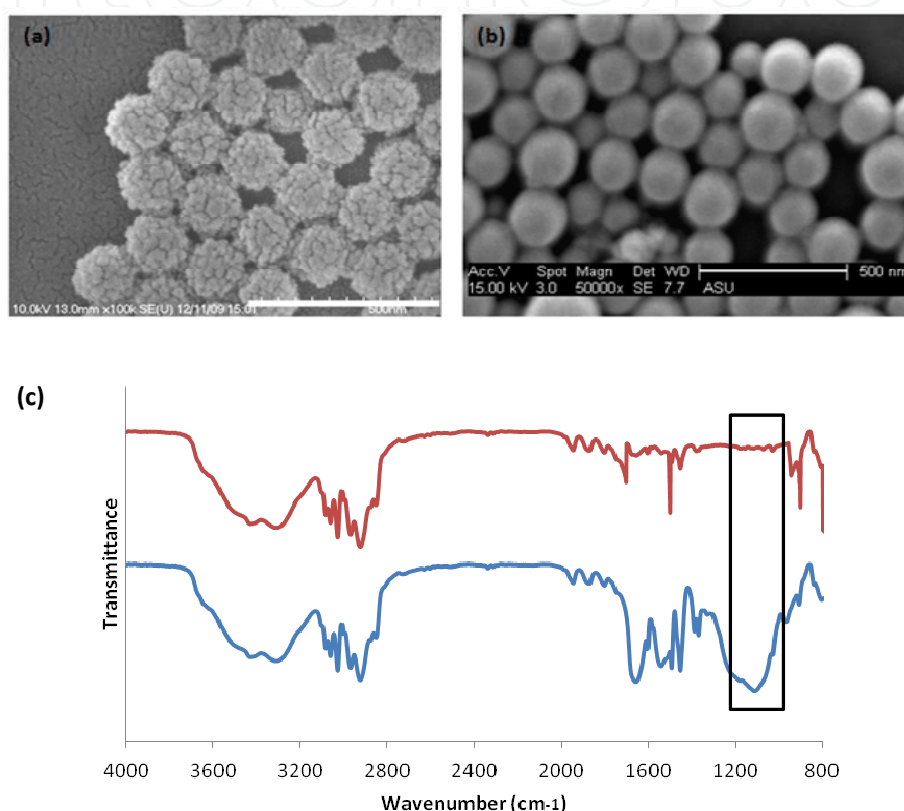


Fig. 7. (a) An SEM image of the composite particles; (b) SEM image taken after HF etching process (the scale bar represents 500 nm); (c) An FTIR spectrum of the composite nanoparticles where the blue line represents the composite particles and the red line is a sample of composite particles treated with HF. The box highlights the difference between the two spectra near 1104 cm^{-1} , which corresponding to the asymmetrical vibration of the Si-O-Si bond the two spectra near 1104 cm^{-1} which corresponding to the asymmetrical vibration of the Si-O-Si bond.

Figure 9(a) shows the dependence of average diameter of the composite particles on temperature with 15% NIPAAm. The average particle size at 25°C is approximately 92 nm. The size decreases sharply as the temperature reaches 32°C, around the LCST for homopolymer PNIPAAm and size change is nearly reversible upon cooling. In addition, we have encapsulated a drug, 17-(Allylamino)-17-demethoxygeldanamycin (17AAG), during the Pickering emulsion polymerization and performed cumulative drug release measurements. Figure 9(b) depicts the cumulative fractional drug release at 25 °C and 40 °C

of 17-AAG from the drug-loaded nanoparticles. No significant release of the drug was observed at room temperature (25°C). However, at a higher temperature of 40°C, the drug

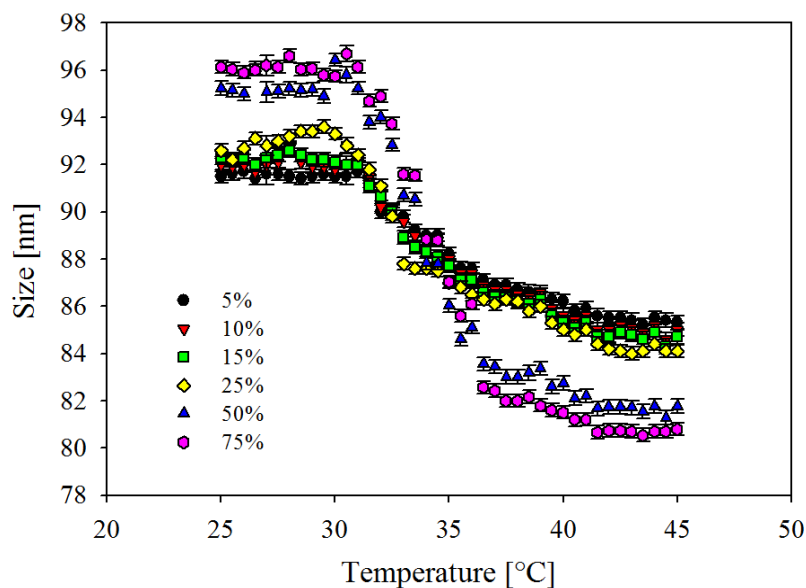


Fig. 8. Hydrodynamic diameters of PS/PNIPAAm-silica composite core-shell nanoparticles measured by DLS, decrease significantly near the transition temperature of PNIPAAm (32°C). The legend shows the various concentrations of NIPAAm, it is observed for higher concentrations of NIPAAm there is greater size change of nanoparticles.

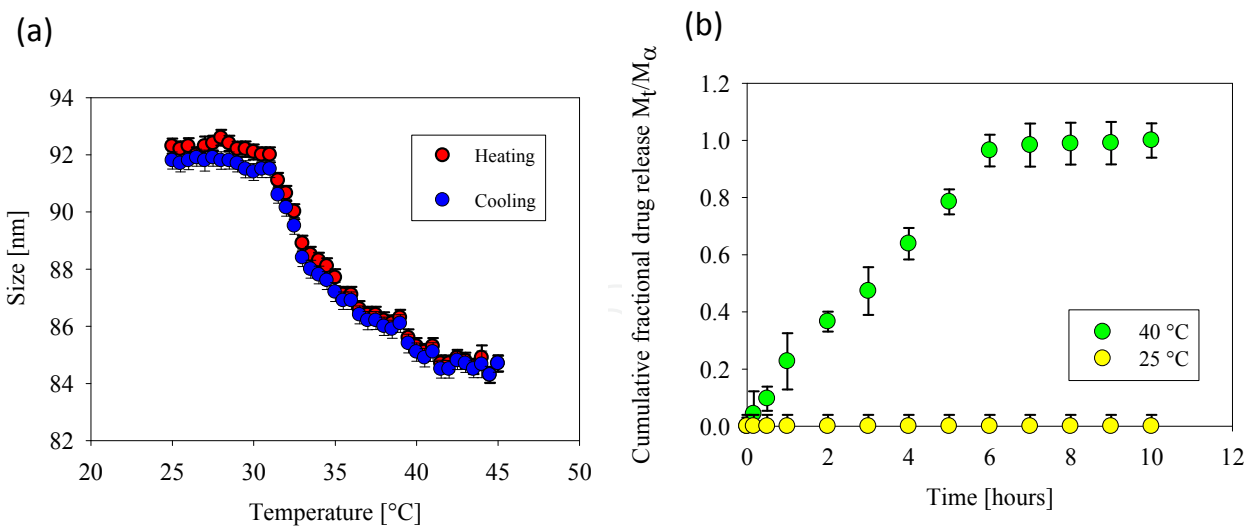


Fig. 9. (a) The dependence of average diameter of composite nanoparticles on temperature. The error bars show standard deviations of particles made in three different batches. The transition temperature is around 32°C. There size transition is nearly reversible; (b) Cumulative fractional drug release versus time curve indicating release at room temperature and at 40 °C. There is minimum release at 25 °C which is below the transition temperature of the nanoparticles.

releases from the nanoparticles reached a maximum after 7 h. The cumulative fractional drug release is calculated as M_t/M_∞ , where t is the release time, M_t is the amount of drug released at a time t and M_∞ is the amount of drug released at time infinity. Infinity is taken to be when the maximum amount of drug gets released and there is no subsequent release after infinity. The concentration of the drug in the sample solution was read from the calibration curve as the concentration corresponding to the absorbance of the solution. To determine the release mechanisms of the composite nanoparticle system an equation proposed by Yasuda et al. was used (Yasuda et al., 1968), which analyses the release behavior of a solute from a polymer matrix, $\frac{M(t)}{M(\infty)} = kt^n$ where k is a constant related to the physical properties of the system, and the index, n , is the diffusional component that depends on the release mechanism. When $n < 0.5$, the solute is released by Fickian diffusion; when $0.5 < n < 1.0$, the solute is released by non-Fickian diffusion and when $n = 1$, there is zero order release [Yasuda et al., 1968]. The calculated n value is 0.73 which indicates the non-Fickian diffusion. The mathematical model indicates that the drug diffusion behavior is non-Fickian and the rate of drug release is due to the combined effect of drug diffusion and polymer response due to increase in temperature.

4. Conclusion

In summary, polystyrene-silica core-shell composite particles were successfully synthesized by a novel one-step Pickering emulsion polymerization. The sole stabilizing effect of silica nanoparticles in the emulsion polymerization was verified. In addition, possible mechanisms of Pickering emulsion polymerization were explored and suggested that homogeneous coagulative nucleation is likely the dominating mechanism here. Finally, the temperature responsiveness of core-shell composite nanoparticles and drug release were validated by incorporating NIPAAM as a co-monomer into the Pickering emulsion polymerization.

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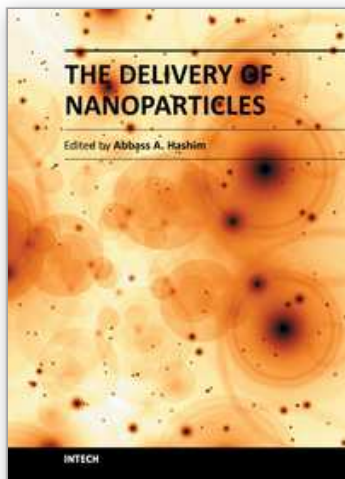
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Nanoparticle is a general challenge for today's technology and the near future observations of science. Nanoparticles cover mostly all types of sciences and manufacturing technologies. The properties of this particle are flying over today scientific barriers and have passed the limitations of conventional sciences. This is the reason why nanoparticles have been evaluated for the use in many fields. InTech publisher and the contributing authors of this book in nanoparticles are all overconfident to invite all scientists to read this new book. The book's potential was held until it was approached by the art of exploring the most advanced research in the field of nano-scale particles, preparation techniques and the way of reaching their destination. 25 reputable chapters were framed in this book and there were alienated into four altered sections; Toxic Nanoparticles, Drug Nanoparticles, Biological Activities and Nano-Technology.

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