



Preparation of multilayered organic–inorganic hybrid core–shell particles by stepwise surface formation

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ABSTRACT

This paper introduces a stepwise formation method for micro-sized, multilayered core–shell particles comprising an inorganic core, organic inner shell, and inorganic outer shell. A silica core was coated with a polystyrene seed layer, followed by surface seed polymerization with styrene, to afford the inner shell. These particles were then coated with a silica outer shell by a surface sol–gel reaction with tetraethoxysilane. The versatility of this combined surface seed polymerization and sol–gel method is emphasized by the precise control achieved over particle diameter as well as shell thickness and count. Moreover, the organic inner shell can be readily eliminated to afford a single-core-containing micro-capsular structure.

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1. Introduction

There has been considerable recent interest in organic–inorganic hybrid core–shell particles for their many practical applications such in drug delivery, cosmetics, electronic devices, and chemical analysis [1–5]. Firstly, several routes have been explored to coat an inorganic core with an organic shell [4–10]. Among these, surface graft polymerization, in particular, is of wide interest due to its versatility, involving polymerization after the attachment of a polymerization initiation group or polymerizable group on the surface of the core particle [6]. Recently, this method has been successfully used for dense and homogenous grafting of an organic polymer via living radical polymerization [7,8]. Secondly, an organic particle can be coated with an inorganic shell by, most commonly, a surface sol–gel reaction between a metal alkoxide and surface hydroxyl groups on the particle in the presence of a polymer dispersant such as polyvinyl pyrrolidone [11,12]. Other methods such as electroless metal plating and mechano-chemical processes have also been proposed [13,14].

Here we show that the two methods can be successfully combined in stepwise fashion for the preparation of micro-sized, multilayered core–shell particles comprising a silica core, polystyrene inner shell, and silica outer shell (Fig. 1). We also show that our two-step process, i.e., the formation of a polystyrene inner shell by surface seed polymerization and then a silica outer shell by the surface sol–gel

reaction, allows precise control over the hybrid monodisperse structures, particularly over particle diameter and shell thickness and count. We also describe how the inner shell can be easily removed by calcination to afford a single-core micro-capsular structure.

2. Materials and methods

2.1. Materials

Styrene, sodium p-styrene sulfonate (SSS), tetraethoxysilane (TEOS), sodium lauryl sulfate (SLS), cetyl trimethyl ammonium bromide (CTAB), and 2,2'-azobis(isobutyronitrile) (AIBN) were purchased from Wako Pure Chemical Industries Ltd. Silica particles (average diameter, 4.8 μm; Sekisui Chemical), divinylbenzene (DVB; Nippon Steel Chemical; 96%), 3-methacryloylpropyltrimethoxysilane (MAPTS; Chisso), poly(vinyl alcohol) (PVA; GL-03; Nippon Synthetic Chemical Industry), and benzoyl peroxide (BPO; Sigma-Aldrich; 75%) were used without further purification.

2.2. Methods

A seed layer of polystyrene was grafted onto the silica particles by surface graft polymerization according to the method reported by Konno et al. [12]. Briefly, the surfaces of silica particles (20 g) were etched in a 0.1 N-NaOH aqueous solution at 50 °C for 30 min and modified with MAPTS (0.191 g) in a 70% ethanol aqueous solution (180 g) at 70 °C for 24 h. To this was added a solution of styrene (20 g), SSS (0.098 g), and AIBN (0.3151 g) in 280 g of the aqueous

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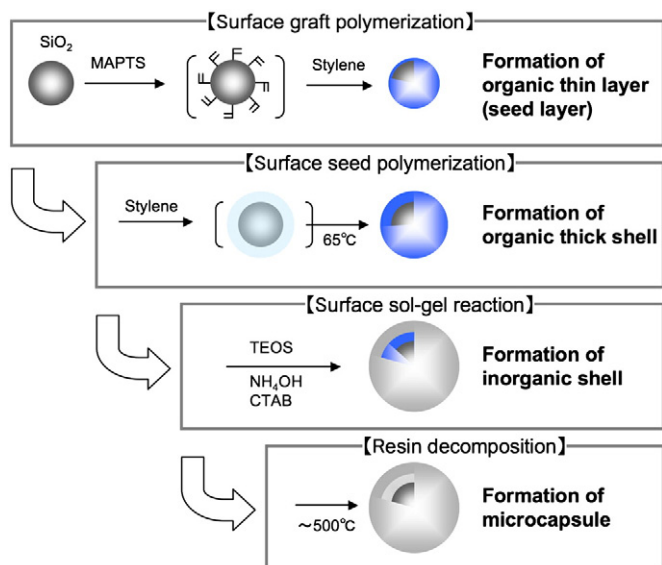


Fig. 1. Schematic illustration for the stepwise preparation method of various organic-inorganic hybrid core-shell particles.

ethanol, followed by stirring at 70 °C for 12 h. Subsequently, the organic shell was grown by surface seed polymerization from the seed layer [15]. Briefly, the silica particles with the seed layer (20 g) were suspended in 100 g of a 10% ethanol aqueous solution containing 0.5 wt.% SLS and 1 wt.% PVA. Then, an emulsion of 30 g monomers (styrene/DVB = 90/10 w/w) and 0.48 g BPO (75%) in 400 g of the ethanol solution containing SLS and PVA was poured into the suspension, followed by stirring for 48 h and heating at 65 °C for 12 h.

The obtained particles were then coated with a silica outer shell by the surface sol-gel reaction according to the previously reported method [16] with a slight modification. Briefly, the particles with the polystyrene shell (5 g) were suspended in 100 g of a 70% ethanol aqueous solution containing 1 wt.% CTAB. After adding a 28% ammonia solution (4 g), a solution of TEOS (15 g) in 100 g of the ethanol solution was dropped into the suspension with stirring at room temperature for 12 h.

A single silica core-containing microcapsule was prepared from the particle with an organic inner shell and inorganic outer shell by heating up to 500 °C (heating rate, 0.65 °C/min) in air and then holding at that temperature for 30 min.

Particle morphology and diameter were examined under a Hitachi S-4800 scanning electron microscope (SEM). Particle cross-sections were obtained by cutting with a microtome (Leica ULTRACUT R) after embedding in an epoxy resin. The percentages of seed layer, organic shell, and inorganic shell were determined with a Seiko 320 thermogravimetry (TG)/differential thermal analyzer (DTA).

3. Results and discussion

3.1. Formation of the polystyrene inner shell on silica core

In this study, we aim to produce the multi-layered particles for practical applications such as energy transduction, cosmetic and construction materials. For this purpose, we used the micron size silica particles with narrow distribution (4.8 μm, coefficient of variation (CV) = 0.6%) as core particles. The shell thickness and the distribution obtained can be easily evaluated by using mono-dispersed particles.

3-Methacryloylpropyltrimethoxysilane (MAPTS) was grafted onto the surface of silica particles. Excess 3-methacryloylpropyltrimethoxysilane (MAPTS) left after the introduction of the polymerizable group was not removed before surface graft polymerization of styrene was performed (Fig. 2(c)). TG analysis confirmed that the seed layer was indeed formed (Fig. 2(c)) and that the formation rate increased with the amount of MAPTS used. These results confirm that the number of methacryloyl groups attached to the surface of the silica particles increases with the amount of MAPTS added and this increases the opportunities for subsequent graft polymerization. Furthermore, without the polymerizable group, no polystyrene layer was observed (Fig. 2(b)). This further confirms that surface graft polymerization can be initiated from the modified surface.

In surface seed polymerization, monomers are absorbed on to the prepared seed layer and are continuously polymerized, thus increasing particle size. The amount of monomer for surface seed polymerization (styrene/DVB = 90/10 w/w) was set at 100, 150, and 200 wt.% with respect to the silica particles. As shown in Fig. 3, the formation rate of the organic shell increased with the concentration of monomer in the emulsion, leading to larger particle diameters with uniform dispersity. TG analysis revealed that the ratio of the organic layer to the silica in the coated particles was 128 wt.% when 200 wt.% of monomer was used. Moreover, the amount of monomer absorbed in the seed layer was more than 20 times the weight of the seed layer. Thus clearly, the seed layer can absorb a large amount of monomer, sufficient to form an organic shell with a thickness on the order of micrometers.

3.2. Formation of silica outer shell and microcapsulation

As shown in Fig. 4(a), when adding three times more tetraethoxysilane (TEOS) than silica core particles by weight, the resultant particle diameter increased from 6.84 μm to 8.05 μm. Since coefficient of variation (CV) before and after silica shell formation were 5.7% and 5.2%, respectively, it is roughly concluded that uniform silica shell could be formed, maintaining good mono-dispersity.

The removal of the organic inner layer was carried out by calcination procedure at 500 °C. As shown in Fig. 4(c), a capsular structure containing

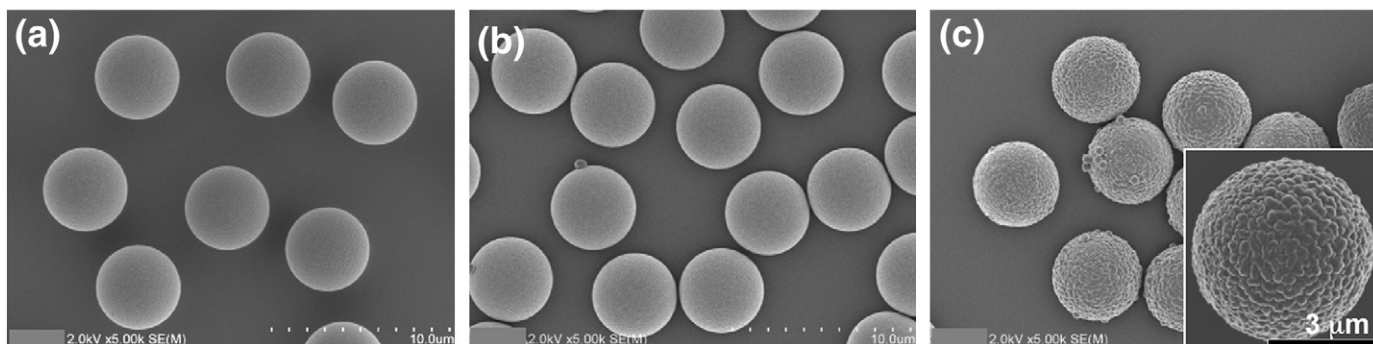


Fig. 2. SEM images of silica particles as core materials and those with seed layers prepared by surface graft polymerization. (a) Silica particles without any treatment. The MAPTS amounts immobilized were (b) 0 wt.% and (c) 9.5×10^{-3} wt.% with respect to the silica core particles. (c) The amount of the seed layer prepared was 5.49 wt.% with respect to the silica core particles.

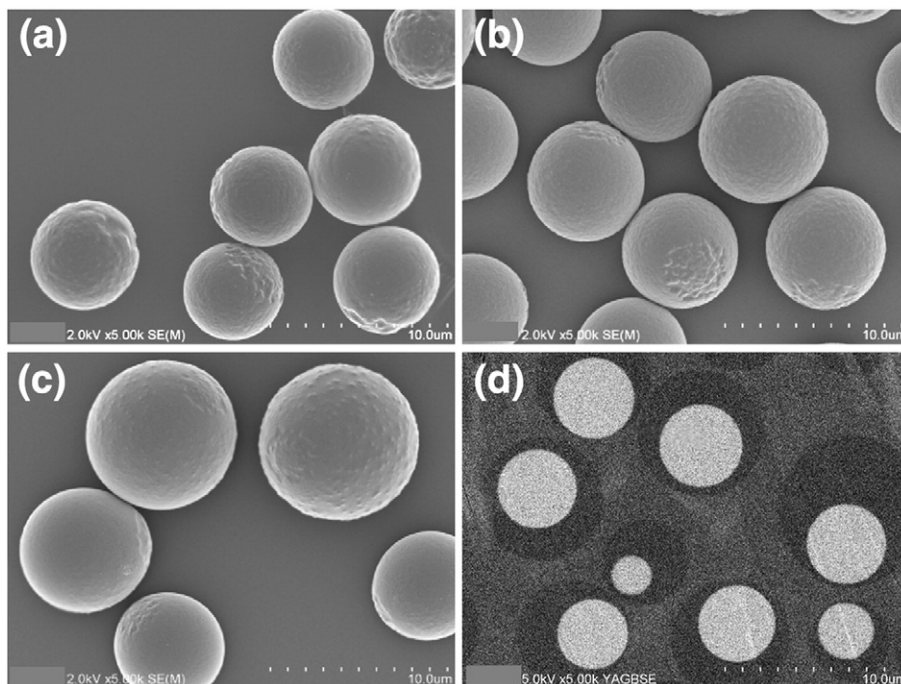


Fig. 3. SEM images of (a, b and c) the silica particles with polystyrene shells prepared by surface seed polymerization and (d) the cross-section of the particles of b. The amounts of the swelling monomers from styrene-DVB (9:1) were (a) 100 wt.%, (b and d) 150 wt.%, and (c) 200 wt.% with respect to the amount of silica core particles, respectively. The average diameter and CV were (a) 6.19 μm and 5.7%, (b) 6.84 μm and 5.7%, and (c) 7.16 μm and 4.6%.

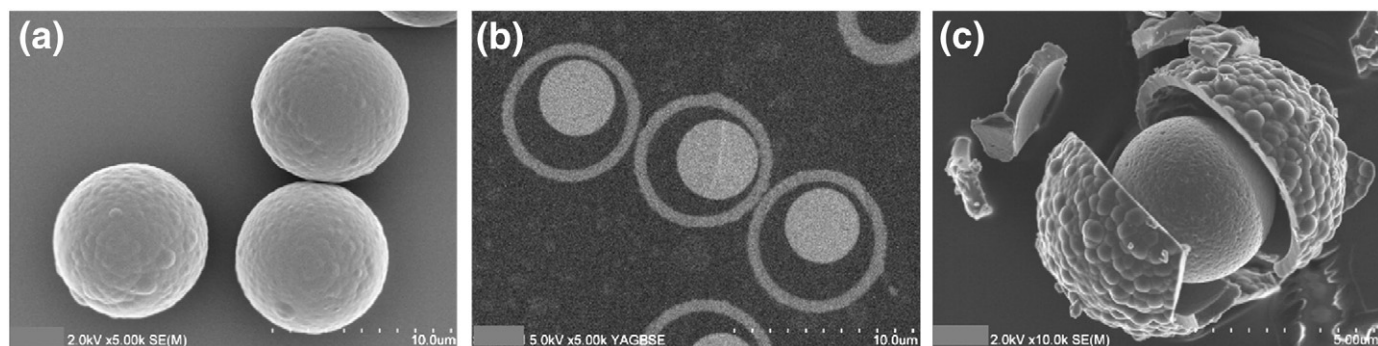


Fig. 4. SEM images of (a) the multilayered particle with silica outer shell prepared by surface sol-gel reaction (the average diameter and CV: 8.05 μm and 5.2%), (b) cross-section of the particle and (c) microcapsular structure particles after removal of organic inner shell (at 500 °C) and milling with mortar.

a single silica particle can be created and it is obvious that the organic inner shell can be completely removed by decomposition.

4. Conclusions

We have established a versatile preparation method for micro-sized, multilayered hybrid core-shell particles. This method is based on the combined use of modified surface seed polymerization and surface sol-gel reaction methods and has the significant advantage that particle diameter and shell thickness can be precisely controlled. The other advantage is that a calcinated single silica core-containing microcapsular structure can be also produced by removing the inner organic shell.

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