



## Colloidosomes: Synthesis, properties and applications



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### ABSTRACT

Colloidosomes represent a rapidly expanding field with various applications in microencapsulation, including the triggered release of cargoes. With self-assembled shells comprising colloidal particles, they offer significant flexibility with respect to microcapsule functionality. This review explores the various types of particles and techniques that have been employed to prepare colloidosomes. The relative advantages and disadvantages of these routes are highlighted and their potential as microcapsules for both small molecule and macromolecular actives is evaluated.

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### 1. Introduction

Colloidosomes are microcapsules whose shells are composed of colloidal particles [1]. In recent years such superstructures have received considerable attention because of their potential importance in the area of microencapsulation. Microencapsulation enables the controlled release of active ingredients in various industrial sectors such as medicine, food, home and personal care products, agrochemicals and cosmetics, enabling the delivery of a range of actives such as drugs, pesticides and fragrances [2–6]. Routes to colloidosomes are most commonly based on the self-assembly of colloidal particles at the interface between two immiscible liquids, typically water and oil. The initial self-assembled structures are known as Pickering emulsions [7] and have been recognized for over a century. Many examples of colloidal particles such as silica sols [8,9] and polystyrene latexes [10] have been shown to be effective Pickering emulsifiers. Stimulus-responsive particulate emulsifiers have also been developed, with inversion or demulsification being achieved in response to changes in solution pH [11,12] or temperature [13]. The preparation of colloidosomes requires a mechanism for shell reinforcement at the interface to convert the Pickering emulsion precursor into robust microcapsules that can survive removal of the oil/water template. In this review, we summarize the various techniques employed to prepare stable colloidosomes and highlight their suitability and potential uses as microcapsules, as well as identifying current technical problems (see Fig. 1).

The first colloidosome-type structures were reported in a series of three papers by Velev and co-workers in 1996, who employed *n*-octanol droplets as templates for latex self-assembly [14–16]. Formation of both hollow spherical ‘supraparticles’ [14] whereby latex particles were adsorbed at the water/oil interface (see Fig. 2) and also ‘ball-like aggregates’ [15] in which the latex particles penetrated the oil droplet interior were described. It was found that using anionic sulfate-stabilized polystyrene latex particles alone did not produce stable emulsion droplets. Instead, the latex had to be ‘sensitized’ via adsorption of an amino acid (lycine) to promote sufficient interfacial activity. A strong coagulant (casein, HCl and CaCl<sub>2</sub>), which was known to cause latex aggregation in bulk aqueous solution, was then added to ‘lock in’ the latex particle monolayer surrounding the droplets. This additional stabilization enabled the resulting microcapsules to survive removal of the *n*-octanol phase on treatment with excess ethanol. The third paper in the series reported an inverted water-in-oil formulation, whereby the same sensitized anionic latex particles were self-assembled around water droplets [16] suspended in *n*-octanol. In order to achieve this phase inversion a relatively high volume fraction of *n*-octanol (0.94) was used. This formulation produced more monodisperse droplets compared to the previous two papers.

### 2. Colloidosome preparation via thermal annealing

The term ‘colloidosome’ was first introduced by Dinsmore et al. [17], who prepared microcapsules via self-assembly of micrometer-sized carboxylated polystyrene latex particles at the surface of oil-in-water (o/w) or water-in-oil (w/o) emulsion droplets. Once the droplet surface was fully covered by particles, the colloidosome shell was formed by sintering the latex particle monolayer. This

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was achieved by heating the emulsion to just above the  $T_g$  of the polystyrene latex particles ( $\sim 105^\circ\text{C}$ ) in order to fuse them together. Since this latex  $T_g$  exceeds the boiling point of the aqueous continuous phase, this approach necessitated the addition of 50% glycerol to raise the boiling point and hence minimize evaporation. Water-in-oil colloidosomes could be transferred to a water-continuous phase by gentle centrifugation. SEM studies indicated that the interstitial gaps between adjacent fused particles could be controlled by varying the sintering time. The authors suggested that this enabled the permeability of the microcapsules to be tuned, although this aspect was not demonstrated. Extending this seminal study, Hsu et al. [18] also reported sintering as a means of ensuring the structural integrity of colloidosomes. After heating to  $105^\circ\text{C}$  for 2 h, individual particles were no longer discernible via SEM, which suggested that the sintering process was complete and a fully-annealed latex shell was formed.

These early examples of colloidosome formation via latex sintering required relatively high temperatures and addition of co-solvent to prevent evaporation of the aqueous continuous phase. However, this approach is likely to be detrimental for the encapsulation of thermally-sensitive actives such as fragrances or drugs. One solution to this technical problem is to replace polystyrene latex with a lower  $T_g$  copolymer latex, thus allowing a reduction in the sintering temperature. Accordingly, Routh and co-workers [19,20] utilized a poly(styrene-co-*n*-butyl acrylate) latex to prepare 2–5  $\mu\text{m}$  diameter w/o emulsions and, after heating to  $35\text{--}65^\circ\text{C}$ , robust colloidosomes with aqueous cores (see Fig. 3). In this particular example, the copolymer latex alone was not an efficient Pickering emulsifier, hence a suitable oil-soluble co-surfactant (Span 80) was required to optimize colloidosome formation.

Laib and Routh [19] identified a technical problem when preparing colloidosomes via thermal annealing. In addition to the desired

intra-shell latex sintering, latex sintering between neighboring colloidosomes can occur, leading to extensive inter-colloidosome fusion. This is particularly problematic at high solids and hence is a potential barrier to scale-up syntheses. However, Salari et al. [21] overcame this problem by adding poly(styrene-block-ethylene-co-propylene) (PS-EP) diblock copolymer micelles to a Pickering emulsion prior to annealing so as to act as an additional steric stabilizer. In this work, the original polystyrene particles used to prepare the Pickering emulsions were synthesized via soap-free emulsion polymerization. This latex was then emulsified with *n*-decane in the presence of salt to give a water-in-oil emulsion. The PS-EP copolymer micelles were then added to the Pickering emulsion and heated to  $50^\circ\text{C}$ . The *n*-decane oil phase has a plasticizing effect on the polystyrene latex, allowing sintering to occur below its normal  $T_g$ . It was found that significant colloidosome fusion occurred in the absence of the PS-EP micelles, whereas particle aggregation was reduced substantially if this diblock copolymer was added prior to latex sintering.

### 3. Polyelectrolyte complexation and layer-by-layer deposition

In addition to preparing colloidosomes via latex sintering, Dinsmore et al. [17] also examined electrostatic adsorption of an oppositely-charged polyelectrolyte as a means of reinforcing the latex superstructure via physical cross-linking. More specifically, a high molecular weight cationic poly(L-lysine) was adsorbed onto the surface of Pickering emulsions prepared using anionic polystyrene latex particles. This approach proved to be very effective: robust colloidosomes were produced which were much more flexible and deformable compared to the relatively brittle microcapsules produced via latex sintering. This polyelectrolyte adsorption method was further developed by Gordon et al. [22] The latex

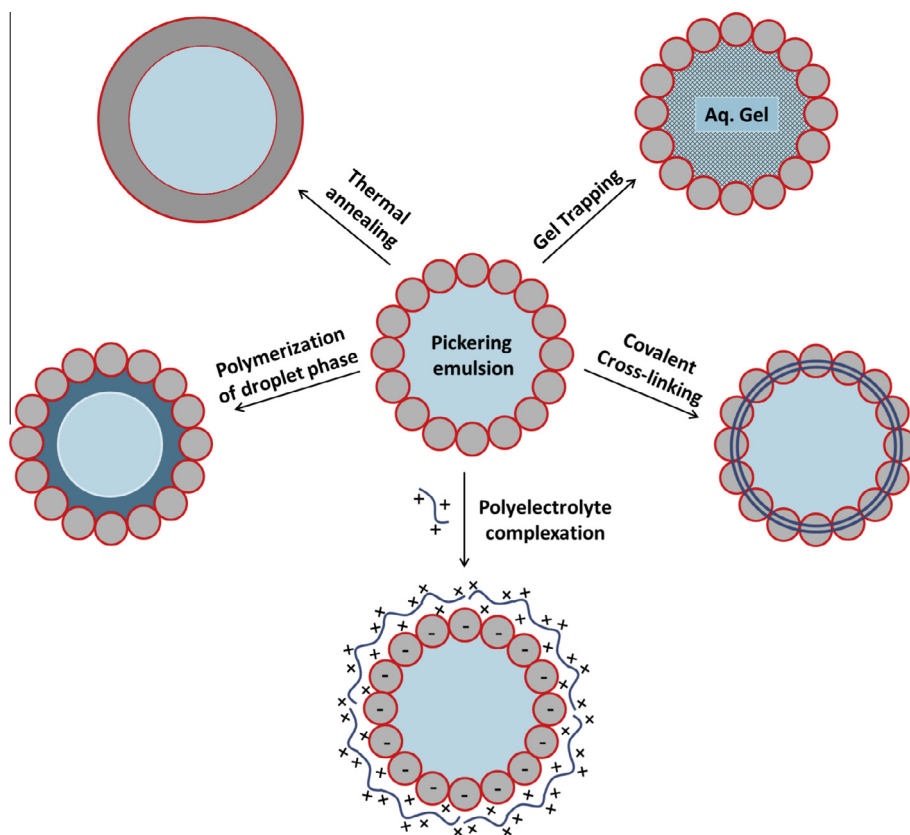


Fig. 1. Summary of the various routes investigated for the preparation of colloidosome microcapsules via self-assembly of colloid particles at the oil/water interface.

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