



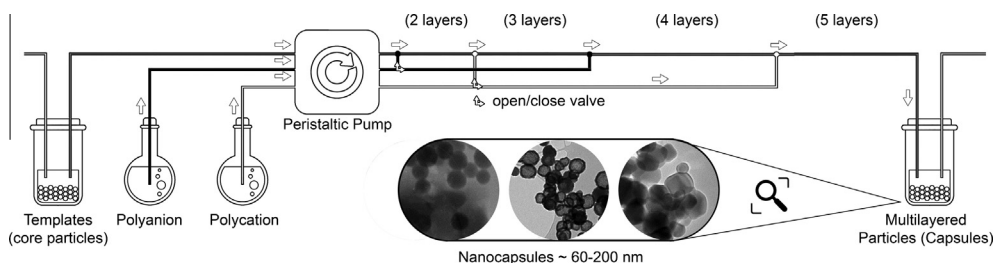
# Fabrication of polyelectrolyte multilayered nano-capsules using a continuous layer-by-layer approach



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## GRAPHICAL ABSTRACT



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## ABSTRACT

The layer-by-layer approach is a highly versatile method for the fabrication of multilayered polymeric films and capsules. It has been widely investigated in research for various polyelectrolyte pairs and core template particles. However, the fabrication of nano-sized capsules at the larger scale is difficult and time consuming, due to the necessity of washing and centrifugation steps before the deposition of each polyelectrolyte layer. This results not only in a very long fabrication time, but also in the partial loss of particles during those intermediate steps. In this study, we introduced a continuous approach for the fabrication of multilayer polyelectrolyte based nano-capsules using calcium phosphate core nanoparticles and a tubular flow type reactor with the potential for synthesizing tens of milligrams of capsules per hour. Adsorption of the polyelectrolyte layer occurred in the tubing where particles and polyelectrolyte solution of choice were mixed, creating a layer of polyelectrolyte on the particles. After this, these newly surfaced-modified particles passed into the next segment of tubing, where they were mixed with a second polyelectrolyte of opposite charge. This process can be continuously repeated until the desired number of layers is achieved. One potential problem with this method concerned the presence of any excess polyelectrolyte in the tubing, so careful control of the amount of polymer added was crucial. It was found that slightly under dosing the amount of added polyelectrolyte ensured that negligible unadsorbed polyelectrolyte remained in solution. The particles created at each deposition step were stable, as they all had a zeta potential of greater than  $\pm 25$  mV. Furthermore the zeta potential measurements showed that charge reversal occurred at each stage. Having achieved the necessary number of polyelectrolyte layers, the calcium phosphate cores were easily removed via dissolution in either hydrochloric or acetic acid.

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## 1. Introduction

The deposition of materials of opposite charge sequentially onto surfaces or particles has become increasingly well studied in recent

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decades. The original studies date back to the work of Iler [1] fifty years ago, who deposited alternating layers of positively-charged silica and negatively-charged boehmite onto flat charged surfaces. Surprisingly, the work remained largely in abeyance for twenty five years and it was not until Decher et al. adapted the approach to coat oppositely charged surfaces with polyelectrolyte multilayers [2–4] which led to extensive study in this area. This method was later used to coat colloidal particles [5–7] and subsequently construct microcapsules [8,9]. The microcapsules were prepared by the stepwise adsorption of polyelectrolytes onto charged colloidal template particles, before the removal of the core particles via dissolution in acid. This fabrication technique allowed for control over the capsule size (by controlling the core template size), the capsule wall thickness (by controlling the number of polymer layers), and the capsule wall composition. This process has now emerged as a simple, versatile and inexpensive technique for the construction of polymeric thin films on both surfaces and particles. This methodology has been used in many studies to prepare capsules of different sizes using various polymer pairs (not all involving opposite charged polyelectrolytes) and core template particles. However, there are a number of associated issues with this technology. Firstly, although the preparation of micron-sized capsules has been met with relative ease, the fabrication of nanosized capsules has proved to be a challenge [10–12]. Micron sized particles using melamine cores were originally used because the core can be easily removed via the immersion in acid, however difficulty arose with particles less than 100 nm in size, because the core particles that small were unavailable [7–9,13–18]. Fabrication of smaller capsules is possible with the use of silica or polystyrene particles as core templates, but complete removal of the core is problematic [19–23]. Polystyrene is commonly dissolved by immersing the coated particles in tetrahydrofuran, THF, which is both miscible with water and a strong solvent for polystyrene. However, the polystyrene would need to diffuse through the polyelectrolyte film and whether complete dissolution occurs whilst maintaining the integrity of the polyelectrolyte film is uncertain.

Another issue related to the layer-by-layer manufacture of nano-capsules, concerns the time consuming, labour intensive method currently used for producing the capsules, which inhibits their use in any large scale commercial application. The commonly practiced procedure involves mixing the core particles with a dilute polyelectrolyte solution until the adsorption of the polyelectrolyte is complete. The resulting suspension is then centrifuged and the particles redispersed in water, before the process is repeated a further two, or three, times to ensure removal of any unadsorbed polyelectrolyte. The entire procedure is then repeated for the addition of every polyelectrolyte layer. As well as being time consuming, each centrifugation/redispersion cycle inevitably leads to the partial loss of particles, so that after 10–20 cycles, not many particles remain, even before the core removal process occurs.

A number of authors have proposed various solutions to these problems. Voigt et al. [16] developed a method of layer-by-layer polyelectrolyte adsorption on core latex particles by means of semi-continuous membrane filtration. This method produced high quality microcapsules due to reduced particle aggregation, but required constant control and repeated manual adjustments, which make scaling-up a challenge. Kantak et al. [24] presented a “microfluidic pinball” technique for the continuous generation of microcapsules, which involved the microfluidic production of oil droplets. The droplets were guided along a row of micropillars and through three parallel laminar streams – two polymer solutions and one washing solution. This method, however, was only capable of producing a relatively small number of capsules. Richardson [25] presented an automated capsule preparation approach, whereby the core particles were immobilised in a gel

film which was then clamped and dipped into different polyelectrolyte and rinsing solutions. The gel was then melted and the particles recovered, however again only a few particles can be made at any one time. Later, Richardson introduced another method based on the utilisation of immobilised particles in a hydrogel [26], in a process called electrophoretic polymer assembly. The hydrogel-particle substrate was placed between two electrodes so that the polyelectrolyte solution travelled through the hydrogel-particle substrate from anode to cathode or vice versa, depending on the polyelectrolyte charge. Richardson also developed a method called convective polymer assembly [27], that involved using immobilised particles in a hydrogel and convection to move the polyelectrolyte solutions through the gel. However, once again, only a small number of capsules can be made using this method. One of the more recent methods for the fabrication of layer-by-layer capsules was developed by Björnalm et al. [28], and is a solely flow-based technique which used tangential flow filtration to aid the removal of excess polyelectrolyte from the system.

The method we present in this paper addresses the common issues associated with the layer-by-layer technique, but from a novel perspective. We have investigated the build-up of the polyelectrolyte multilayers [29–35] onto the core particles using a tubular type reactor, whereby polyelectrolytes of opposite charge are introduced at different points along a tube. One problem that was anticipated in this work was the presence of excess polyelectrolyte following the adsorption process. However, it is known that polymers and polyelectrolytes exhibit a high affinity type adsorption isotherm, where initially almost all the added polymer adsorbs to a surface of a particle, and only in the final stages, does any excess polymer remain in solution [36–40]. Therefore, precise control over the concentration ratio of the added polymer to core particles may allow for the buildup of multilayers of the polyelectrolyte, without any significant polyelectrolyte complexation issues. Hence, the aim of this work was to investigate the hypothesis by deliberately using fractionally less polyelectrolyte than would be required to reach saturation conditions. We show that it is possible to produce nano-capsules at a flow rate of 600 ml of colloidal suspension per hour, enabling relatively large quantities of capsules to be easily prepared. More significantly, we suggest an approach for the future large-scale, commercial production of nano-capsules prepared from alternating layers of charged materials.

## 2. Experimental section

### 2.1. Chemicals

Two types of core particles, both comprised of calcium phosphate coated with a positively charged polyelectrolyte, were prepared. For the first type of particles, the following materials were used: poly(diallyldimethylammonium chloride) (PDADMAC, average  $M_w$  100,000–200,000 (low molecular weight), 20 wt% in  $H_2O$ , Sigma–Aldrich), calcium L-lactate hydrate ( $\geq 98\%$  KT calc. based on dry substance, water  $\sim 4$  mol/mol, Sigma–Aldrich, Gillingham, Dorset), ammonium phosphate (Hopkin & Williams Ltd). The same set of materials was used for the second type of core particles, except that the polyelectrolyte – PDADMAC was replaced with  $\epsilon$ -Poly-L-Lysine (96.3%, Handary Epolylly™ HCl, Ultrapure). Three polyelectrolyte pairs were used for layering in order to fabricate multilayered capsules. The first pair was poly(sodium-4-styrenesulfonate) (PSS, average  $M_w \sim 70,000$ , Sigma–Aldrich, Gillingham, Dorset) and poly(diallyldimethylammonium chloride) (PDADMAC, average  $M_w$  100,000–200,000 (low molecular weight), 20 wt% in  $H_2O$ , Sigma–Aldrich, Gillingham, Dorset), the second pair was the poly(diallyldimethylammonium chloride) and lambda

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