EVAPORATION-INDUCED SELF-ASSEMBLY OF UNIFORM SILICA MICROPARTICLES WITH MESOSCOPIC STRUCTURES VIA SPRAY DRYING

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ABSTRACT
The properties of particles formed during spray drying are largely determined by the properties of the precursors and the drying conditions. The thermal and mass transfer histories significantly affect the structure formation (and subsequent functionality) and the processes are indeed very complex, particularly when dealing with polydisperse droplets as in conventional spray dryers. Here a more systematic study is done using a microfluidic spray drying approach capable of generating monodisperse particles. We observed the formation of uniform silica microparticles with unique mesoscopic structures from colloidal silica nanoparticles and a hydrophilic polymer (sodium alginate) via microfluidic spray drying. A buckling-driven shape transition of the initial spherical droplets took place in all the observed cases during the evaporation induced self-assembly. The mesoscopic architectures and surface features of the microparticles were shown to be strongly dependent on the mass fraction of the polymer incorporated in the initial precursors, but were independent of the mass fraction of silica nanoparticles (2% to 10% range) in the droplets. The formation of sub-micron aggregates was noticeable with increasing ratio of added polymer in the droplets. However, the phenomena of shape deformation and buckling were found to be less significant at a lower drying rate.

INTRODUCTION
As an indispensable industrial process, spray drying has been widely used in various areas, such as food, pharmaceutical, and catalyst production (Masters, 1991). Recently, spray drying has gained greater scientific attention due to its use in the research into evaporation induced self-assembly to synthesize novel functional materials (Dierendonck et al, 2010; Lee et al, 2010). One of the challenges associated with spray drying is the control over particle morphology which could affect both the post-treatment process and the functionalities of the final products (Masters, 1991; Sugiyama et al, 2006). This challenge generally originates from two aspects: firstly, a lack of understanding of drying mechanisms dependent on precursor compositions and drying conditions, especially for complex fluids (such as polymer solutions and colloidal suspensions) (Pauchard & Allain, 2003); and secondly, most conventional atomizers produce polydisperse droplets which experience various drying profiles thus resulting in particles with different morphological properties, even within the same drying conditions (Iskandar et al, 2003).
In the drying of colloidal suspension, fluid and elastic behaviors of the drying droplets inducing deformation are always encountered for the final particles (Tsapis et al., 2005; Chen & Evans, 2009). Studies have shown that the buckling is generally caused by the emergence of particle-dense regions at the surface of the droplet (i.e. a viscoelastic shell formed by the evaporation induced self-enrichment of nanoparticles) before the end of drying (Sugiyama et al., 2006). With further solvent evaporation, the capillary forces which drive the deformation of the shell surpass the electrostatic forces stabilizing these nanoparticles, hence causing deformation producing particles with non-spherical shapes (Tsapis et al., 2005; Sen et al., 2010). The shell formation process that could be influenced by the droplet drying rate, the amount of colloidal particles in the initial droplets, and the inter-particle forces of the colloidal particles, play a critical role in determining the final particle morphology.

In this study, we report the evaporation induced self-assembly of colloidal silica nanoparticles during spray drying for a range of concentrations, drying rates, and interparticle interactions. Different drying rates were realized by the use of different drying temperatures and solvents with different thermal properties. Specific amounts of sodium alginate (hydrophilic polymer) were added into the precursor. A novel microfluidic spray drying technique producing highly monodisperse microparticles was employed to exclude the influence of polydisperse droplets (size and trajectories). A direct relationship between the precursor properties and drying conditions to the final particle morphology could thus be observed for the first time.

**EXPERIMENTAL SECTION**

**Materials**

LUDOX® HS-30 colloidal silica (30% solid suspension of SiO$_2$ nanoparticles with an average particle size of 12.0 nm ± 0.7 nm as measured by dynamic light scattering, Sigma-Aldrich, Australia) and alginate sodium salt (sodium alginate, low viscosity: 20-40 cps) were purchased from Sigma-Aldrich (Australia). Acetone was of analytical grade from Merck (Australia). Deionized water (Milli-Q) was used for all precursor preparation.

**Particle fabrication and characterization**

The precursors for spray drying were prepared by directly dispersing a specific amount of colloidal silica into the solvent. To investigate the effects of colloidal concentration, solvent and polymer additive, different formulations of the precursors were prepared (Tab.1).

Spray drying of the colloidal suspensions was carried out using a specially designed microfluidic spray dryer (Wu et al., 2009, 2010). Monodisperse droplets were generated from precursor solution by a micro-fluidic aerosol nozzle system, with an orifice diameter of 75 µm. Briefly, the precursor solutions were fed into a standard steel reservoir and dehumidified instrument air was used to force the liquid in the reservoir to jet through the nozzle. The liquid jet was broken into droplets by disturbance from vibrating piezoceramics. The droplet formation mode was monitored by a digital SLR camera (Nikon, D90) with a speed-light (Nikon SB-400) and a micro-lens (AF Micro-Nikkor 60mm f/2.8D). The liquid flow rate and applied disturbance frequency were adjusted to best achieve monodisperse droplet formation (Wu et al., 2009). The typical
flow rate and disturbance frequency used in this study for monodisperse droplet
generation were around 1.15g/min and 12000HZ, respectively. The high-speed
photographs of the monodisperse droplets generation process were shown in Fig.1.
These monodisperse droplets obtained were well dispersed and dried at a specific drying
temperature. In a typical experiment, the inlet temperature was kept at 165°C (outlet
temperature 136°C). Inlet temperatures of 235°C and 85°C (with corresponding outlet
temperature of 161°C and 68°C) were also used for a few specific formulations to
investigate the influence of drying temperature on the morphology of microparticles.

Tab. 1: Compositions of the precursors for spray drying

<table>
<thead>
<tr>
<th>No.</th>
<th>Colloidal Silica (w/v)</th>
<th>Alginate (w/v)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.0%</td>
<td>--</td>
<td>H₂O</td>
</tr>
<tr>
<td>B</td>
<td>1.9%</td>
<td>0.1%</td>
<td>H₂O</td>
</tr>
<tr>
<td>C</td>
<td>1.5%</td>
<td>0.5%</td>
<td>H₂O</td>
</tr>
<tr>
<td>D</td>
<td>1.0%</td>
<td>1.0%</td>
<td>H₂O</td>
</tr>
<tr>
<td>E</td>
<td>2.0%</td>
<td>--</td>
<td>Acetone:H₂O / 2:1</td>
</tr>
<tr>
<td>F</td>
<td>10.0%</td>
<td>--</td>
<td>H₂O</td>
</tr>
</tbody>
</table>

Fig. 1: Generation of monodisperse droplets (scale bar: 2mm)
To further confirm that the evaporation induced self-assembly occurred, a droplet (2µL) of specific formulations (i.e. precursors with different colloidal silica/alginate ratios) was placed onto a silicon chip and air-dried under room temperature. The morphology and structure of the spray dried microparticles, as well as the air-dried droplets were characterized by field-emission scanning electron microscopy (FESEM, JEOL 7001F, Japan).

**RESULTS AND DISCUSSION**

Uniform microparticles were successfully prepared from all prepared precursors using the microfluidic spray drying technique. The influences of different precursor compositions and drying conditions on the morphological properties of the spray dried microparticles are discussed below.

**Effect of mass fraction of alginate**

Interparticle forces play an important role in determining the buckling behavior of suspension droplet (Sugiyama et al, 2006). Polymers are common components used in spray drying which could alter the interactions among solid particles in colloidal suspensions (Qiu et al, 2008; Singh et al, 2011).

Microparticles spray-dried from precursors with different amounts of alginate were presented in Fig.2 to 5. The incorporation of alginate was shown to alter the drying behavior of colloidal droplets, even at the lowest concentration (0.1%). Microparticles spray dried from colloidal silica nanoparticles suspension displayed pot-like shapes (Fig.2a) with dense internal structure (Fig.2b) and smooth surface (Fig.2c). With increasing amount of alginate, the shape showed enhanced deformation with rougher surface features (Fig.3a, 4a, 5a). With 0.1% of alginate, more dimples started to emerge on the surface of the particles (Fig.3a), compared with the particles without alginate. The inner section of the shell showed rugged textures with some aggregates found in the cross sections (Fig.3b). Several defects were observed on the outer surface of the dimples (Fig.3c and 3d). With 0.5% of alginate (Fig.4), the particles displayed hat-like shapes with wrinkled outer surface. The inner surface, cross sections, and the defects on the outer surface appeared to be consisted of ~ 100 nm aggregates. With 1% alginate (Fig.5), this feature became more noticeable, with the outer surface composed of mainly these nano aggregates (Fig.5d).

![Fig. 2: (a) SEM photos of the spray dried microparticles from 2.0% colloidal silica in water at inlet temperature of 165°C; (b) cross section; (c) outer surface](image)
Fig. 3: (a) SEM photos of the spray dried microparticles from 1.9% colloidal silica and 0.1% alginate in water at inlet temperature of 165°C; (b) cross section; (c) outer surface; (d) close-up of the section as indicated in c

Fig. 4: (a) SEM photos of the spray dried microparticles from 1.5% colloidal silica and 0.5% alginate in water at inlet temperature of 165°C; (b) inner surface; (c) cross section; (d) outer surface
Fig. 5: (a) SEM photos of the spray dried microparticles from 1.0% colloidal silica and 1.0% alginate in water at inlet temperature of 165°C; (b) inner surface; (c) cross section; (d) outer surface

Fig. 6: SEM images of air-dried droplets at room temperature containing (a₁) 2.0% colloidal silica with inset a₂; (b₁) 1.9% colloidal silica and 0.1% alginate with inset b₂; (c₁) 1.5% colloidal silica and 0.5% alginate with inset c₂

To confirm that the nanostructures observed in the microparticles were formed during the drying process, droplets (2µL) of the same precursors were air-dried at room temperature. Images of the residual materials after water evaporation are shown in Fig.6 with a clear trend of aggregate formation observed with the presence of alginate, although the size here was larger than those formed from spray drying. This simple experiment confirmed that the aggregates were likely to be formed by evaporation induced self-assembly during the solvent removal process. The detailed formation mechanism is out of the scope of this paper and is a subject of a future work.
Effect of drying rate

Two different routes were used to tune the drying rate of the colloidal droplets, i.e. changing the solvent or the drying temperature. The mixture of acetone and H$_2$O (2:1, v/v) was used as solvent to investigate the influence of solvent on particle morphology. Acetone was chosen because of the relatively low toxicity and low boiling point (56°C). Comparing the spray-dried particles using H$_2$O and acetone/H$_2$O mixture (Fig. 2 and 7), those from acetone/H$_2$O mixture showed more deformed shape. In addition, few nano-scale pores were observed on the particle surface, while the cross sections remained relatively unchanged. The difference in boiling points and specific heat capacities of different solvents could induce different latent heat of evaporation and drying rates. A faster drying rate resulted in shorter drying time and more extreme drying behavior (i.e. faster heat and mass transfers). Thus the tendency of droplet buckling would be enhanced in a more vigorous drying process.

Fig. 7: (a) SEM photos of the spray dried microparticles from 2.0% colloidal silica in acetone: water mixture of 2:1 ratio at inlet temperature of 165°C; (b) cross section; (c) outer surface

Fig. 8: Spray-dried particles from 1.9% colloidal silica and 0.1% alginate in water at (a) 235°C; (b) 165°C; (c) 85°C
Fig. 8 showed the SEM photographs of the microparticles obtained at different drying temperatures spray dried from 1.9% colloidal silica and 0.1% alginate, with particles of distinct features observed. Microparticles resulted from high drying temperatures (235°C and 165°C) were distinguished by the obvious dimples and cracks on the outer surface (Fig.8a and 8b). Particles dried under inlet temperature of 85°C illustrated smooth and intact outer surface (Fig.8c). When a higher drying temperature was applied, a shell could be formed in a shorter time period. To facilitate further solvent evaporation and to release the increased stress among particles, significant buckling and even macroscopic cracking occurred which induced the dimples and defects observed on the final spray dried particles (Ilett et al, 1995; Wu et al, 2010).

Effect of colloidal silica concentration
In a “two-phase” droplet (water and silica nanoparticles), the internal surface energy inside the droplet could be increased by increasing the colloidal silica concentration, thus resulting in an increase of the droplet stiffness (Iskandar et al, 2003). This effect could help to stabilize the droplet and make them more resistant to buckling. Colloidal silica suspension with a mass concentration of 10% was spray dried with an inlet temperature of 165°C to investigate the influence of colloidal silica concentration on particle morphology (Fig.9). Compared with the particles spray dried from 2% colloidal silica suspensions (Fig.2), the obtained microparticles showed larger particle size (from around 60µm at 2% to 100 µm at 10%). However, the particle morphology displayed very similar morphological features. Thus, changing the colloidal concentration from 2% to 10% in this case was not significant enough to affect the morphological transition during the drying of colloidal droplets.

![Fig.9: SEM photos of the spray dried microparticles from 10.0% Colloidal silica (b. cross section, c. outer surface; solvent: H₂O; inlet temperature: 165°C)](image)

CONCLUSION
The control over morphology of microparticles in relation to different process conditions was investigated by spray drying of colloidal silica nanoparticle suspensions. Microparticles with non-spherical shapes were obtained in all cases, confirming the buckling-driven shape transition during drying of colloidal droplets. The addition of a hydrophilic polymer (alginate) produced distinct mesoscopic features of the microparticles, which was strongly related to the amount of the added polymer. An interesting phenomenon observed for the first time was the formation of sub-micron aggregates within the microparticle structures by evaporation induced self-assembly. In addition, the drying rate and colloidal concentrations in the precursors could be used to adjust the morphological features of the final particles.
REFERENCES


