Assembly of magnetic microcomposites from low pH precursors using a novel micro-fluidic-jet-spray-dryer

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ABSTRACT

Spray drying is a convenient method to produce particles in high yields within a short period of time. The benefits of this technique include efficient uses of energy and solvent, and being a virtually waste-free process that allows for scale-up. A major drawback in conventional spray drying is the polydispersity of the produced particles. Herein, a specially designed spray dryer called micro-fluidic-jet-spray-drier (MFJSD) coupled with a micro-fluidic-aerosol-nozzle (MFAN) could generate droplets in a single trajectory pattern, to produce monodisperse particles. The drying temperature could vary from <90 °C to 300 °C to accommodate heat sensitive materials if necessary. For the first time we investigated the use of MFJSD to generate uniform magnetic microcomposites, specifically focusing on the effects of precursor composition, droplet size, and secondary heat treatment on the final properties of the particles. The presence of silica nanoparticles in the precursor was demonstrated to directly affect the morphology of the particles. Precursor containing silica nanoparticles generated particles with bowl-like shapes due to slower redistribution of solutes to support the particle skeleton during drying. In the absence of silica nanoparticles, the particles were almost perfectly spherical albeit with dimpled surfaces. After being subjected to calcination after drying, iron oxide crystals were found on the particle surfaces accounting for the overall magnetic property of the microcomposites, with lower magnetisation observed for particles containing higher amount of silica.

Keywords: Magnetic microcomposites; Microfluidic drying; Silica nanoparticles; Morphology; Iron oxide

1. Introduction

Magnetic-based particles have been used extensively in diverse sectors, such as biomedical, magnetic separation, and as supports for catalysts. In bio-related applications, magnetic-based particles are often coated with biocompatible and/or polymeric materials. Consequently, low temperature wet-chemistry processes such as sol-gels and co-precipitations are generally the preferred routes to give better control over the particle size distribution. However, these methods require extensive uses of solvent during production, and involve a number of steps post-production for recovery, including washing and drying, during which some of the particles could be lost, resulting in a relatively low yield.

Previously, methods such as flame spray pyrolysis have been used to produce magnetic-based materials (Li et al., 2006). Dry synthesis methods such as spray pyrolysis or spray drying can produce high yields within a short production time and is easy to scale-up. The main step is to evaporate the solvent from the atomized droplets to form particles, or in the case of spray pyrolysis, also inducing nucleation and growth of crystals due to the high temperature (>1000 °C) involved in the process.

We investigated for the first time the use of a novel spray dryer, called a micro-fluidic-jet-spray dryer (MFJSD) (Wu et al., 2007, 2009, 2011a) to produce uniform magnetic microcomposites. The specially designed micro-fluidic-aerosol-nozzle (MFAN) of the dryer could generate monodisperse droplets in a single trajectory pattern, allowing better contacts between droplets and the drying air for a more efficient formation of solid particles with uniform size and morphology. This efficient drying process provides the possibility to operate the dryer at a relatively low temperature range (<90–300 °C), as an alternative technique for the assembly of magnetic or thermal sensitive composites with relatively lower energy consumption and virtually no solvent waste. Previously we have...
demonstrated the use of this dryer to generate various particulate systems, including photoluminescent microcomposites of Eu/silica/lactose (Wu et al., 2011b), polymeric microcomposites for controlled drug release (Liu et al., 2011a, 2011b), and milk protein concentrate (Fang et al., 2011).

To produce the composites via spray drying, we used a precursor system containing iron(III) salt, silica nanoparticles, and lactose to act as a binder. The choice of this system was based on our previous work on photoluminescent particles (Wu et al., 2011b), with the outcome contributing to the protocol to assemble uniform microparticles from a range of precursors, including nanoparticle dispersions. Iron chloride was soluble in acidic solution (Cornell, 1991; Hoskins and Pearce, 1995), thus the use of a low pH precursor helped to avoid nozzle blockage due to precipitation during spray drying. Due to the amorphous characteristics of the spray-dried particles (Wu et al., 2009, 2011b), the particles were further calcined under a nitrogen environment to form magnetic microcomposites. The effects from different precursor mixtures and heat treatment periods on the properties of the microcomposites were also discussed.

2. Experimental

2.1. Materials

Distilled water (18.2–18.3 MΩ·cm⁻¹) was used to prepare aqueous solution. Iron(III) chloride hexahydrate (FeCl₃·6H₂O) powder and HCl (32% concentrate) were obtained from Ajax Fine Chemicals (Australia). Meanwhile, α-lactose monohydrate powder (C₁₂H₂₂O₁₁·H₂O) and Ludox®-LS colloidal silica sol (30 wt%, suspension in water, ±7 nm) were both purchased from Sigma–Aldrich (Australia). All chemicals were of reagent grade and used without further purification.

2.2. Preparation of precursor solution for spray drying

Two different compositions of the precursor solutions for spray drying were prepared, as listed in Table 1. Colloidal silica sol was diluted into 250 ml of distilled water. A volume of 500 ml of 2 M HCl was made by mixing concentrated HCl with distilled water. Specific amounts of FeCl₃·6H₂O powders were dissolved into acid solution and put into a hydrosonic bath for 15 min. The diluted silica aqueous solution was then mixed with dissolved FeCl₃·6H₂O solution, followed by lactose powders as excipient to prepare the FCA precursor solutions with different iron and silica contents. Water was added to make up 1000 ml of solution with the final pH of the precursor of ~1.

2.3. Generation of monodisperse microcomposites

The precursor solution was filled into a 1.5 liter standard steel reservoir and was atomized using the micro-fluidic-aerosol-nozzle (MFAN) atomizing system into the drying chamber of micro-fluidic-jet-spray-dryer (MFJSD), the details of which have been reported by Wu et al. (2007, 2011a). The orifice diameter of the MFAN used in this work was 75 μm, and the drying was conducted by setting the hot air guns at 300 °C. Subsequently the spray-dried particles were calcined at various times to study the effects of calcination process on the properties of produced particles. The calcination process was done in N₂ environment at 450 °C with the heating rate of the calcination chamber set at 10 °C/min. The calcination periods observed were 1 h, 2 h, and 3 h.

2.4. Characterization

The droplet generation was observed with a digital SLR camera (Nikon, D90) with a speed light (Nikon SB-400) and a micro-lens (AF Micro Nikkor 60 mm f/2.8D). Particle morphol-

<table>
<thead>
<tr>
<th>Sample</th>
<th>Droplet</th>
<th>Average Diameter</th>
<th>Particle Size Distribution</th>
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<tr>
<td></td>
<td></td>
<td><strong>Droplets:</strong></td>
<td><strong>Particles:</strong></td>
</tr>
<tr>
<td>FCA1</td>
<td></td>
<td>151 ± 6 μm</td>
<td>72 ± 7 μm</td>
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<tr>
<td>FCA2</td>
<td></td>
<td>157 ± 5 μm</td>
<td>54 ± 5 μm</td>
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**Fig. 1** – Observation of droplet generation and the corresponding spray-dried particle size distribution. Scale bar: 2.5 mm.
ology was observed from the images taken by field emission scanning electron microscope (JEOL 7001F FEG SEM, Japan) at 15 kV. All size distributions were obtained from processing and analysing the images with ImageJ™ (Java) available from http://rsbweb.nih.gov/ij/. The phase composition of the spray-dried particles was examined by a Holland Philips 1140 X-ray diffractometer (XRD) (CuKα radiation with λ = 1.5405 Å). The magnetic properties of the calcined particles were tested by Riken BHV35H Vibrating Sample Magnetometer (VSM) at 5 kOe (room temperature) with a resolution of 10 Oe. Since the samples contained iron, and non-magnetic silica and lactose, the magnetisation value was normalised using the initial amount of iron in the precursors. As the spray drying method produced virtually no waste from uniformly mixed precursors, the presented values should indicate the magnetic property of the iron oxide formed on the microcomposites.

3. Results and discussions

3.1. Morphology of microcomposites after spray-drying

Fig. 1 shows the monodisperse droplets atomized from the MFAN nozzle in a single line and the size distributions of the resulting solid particles. Fig. 2 shows the SEM observation of the spray-dried particles. FCA1 demonstrated bowl-like shape similar to the particles observed in Wu et al. (2011b). On the other hand, FCA2 containing lactose and iron chloride produced particles with ‘golf ball’ morphology, i.e. spherical particles with dimpled surfaces. Both showed narrow particle size distributions with mean particle sizes of 72 ± 7 μm for FCA1 and 54 ± 5 μm for FCA2, respectively.

The same morphology to FCA1 particles (Fig. 3: FCA1) has been observed previously (Wu et al., 2011b), which used a
similar type of precursor. With the addition of silica nanoparticles, the morphology of the particles changed into bowl-like shapes at the drying temperatures observed. Wrinkled and buckled particles have been observed in several studies investigating droplet drying with colloidal precursors using the single drying droplet mechanism (Pauchard and Couder, 2004; Sugiyama et al., 2006; Tsapis et al., 2002, 2005).

This droplet deformation can be better explained through understanding of the drying process (Tsapis et al., 2002; Vehring et al., 2007; Yao et al., 2008). Drying mechanism is affected by droplet evaporation and solute(s) diffusion (Tsapis et al., 2002; Vehring et al., 2007; Yao et al., 2008). Both evaporation and diffusion rates will decrease during drying due to the increase difficulty in removing residual moisture (Tsapis et al., 2002). Initially, the droplets of FCA1 precursor and FCA2 precursor would both shrink isotropically while the shell was formed. However, as the drying progressed, the shell formation for FCA1 precursor may be shorter than FCA2 precursor because silica nanoparticles in FCA1 precursor had smaller diffusion coefficient than lactose molecules. These colloidal contents were concentrated in forming the outer shell of the particles due to the capillary forces (Iskandar et al., 2001; Tsapis et al., 2002; Wang et al., 2007). Therefore, silica nanoparticles would build up on the surface faster, and at certain point position themselves in place by electrostatic or Van der Waals forces to resist further shrinkage (Sugiyama et al., 2006; Tsapis et al., 2002). On the other hand, lactose molecules diffused at the same rate with the droplet evaporation rate and caused slower shell precipitation formation. The evidence that the particles from FCA1 precursor had faster time restriction for shell shrinkage can be seen from the average particle size of FCA1 particles that was larger than particles from FCA2 precursor, although they both experienced the same drying condition. With continuing drying process, the semi-dried FCA1 particles experienced two competing electrostatic forces and capillary forces within the particle shell. Because of this, the particle shell started to buckle/collapse due to the slow solute redistribution, to support the particle skeleton (Lechuga-Ballesteros et al., 2003; Tsapis et al., 2002). In contrast, spherical shape of FCA2 particles was caused by the larger diffusion rate of lactose molecules providing better distribution of solutes on the droplets during the drying process. Hence, FCA2 particles would have higher mechanical strength on their particle skeleton (Tsapis et al., 2002).

More detailed explanation of the mechanisms inducing the distinct shapes of these particles has been reported previously (refer to schematic presented in Fig. 9 of Wu et al., 2011b), although the surfaces of these particles were much

Fig. 3 – SEM images of FCA1 samples at different calcinations time. Scale bar: 10 μm (a and b) and 100 nm (c and d).
smoother. This condition was caused by the different precursor solution systems used. In the current case, iron salt solution was a significant component of the precursor mixture in addition to lactose and silica nanoparticles, while the precursors used in Wu et al. (2011b) were predominantly lactose and contained only a very small amount of europium salt. FCA1 would have a competing evaporation rate for lactose and iron solutions, while also experiencing more complex drying mechanism due to the existence of electrostatic forces from silica nano-particles forming the particle shell. This condition caused the particles to have slightly wrinkled, bowl-like particles.

The spherical shape of particles produced from precursor FCA2 without silica nanoparticles (Fig. 4: FCA2) was probably due to the high content of lactose in the precursor. The dimples were caused by different evaporation rates between lactose solution and iron solution. Without the presence of silica nanoparticles, the droplets of FCA2 were relatively smaller in size. However, with the combination of iron salt and lactose, the drying mechanism would be slightly different from the drying mechanism for lactose-only precursor (Wu et al., 2011b). During isotropic drying, the diffusion rate would be stable between different molecules. However, once the surface enrichment started, different evaporation kinetics took effect. Lactose molecules would evaporate slower than iron solution with lower diffusion rate. As the drying progressed, precipitation of separate phase was initiated to form the particle shell. These phase-separated domains continued to accumulate on the surface, while also beginning to merge during shell thickening. Different solute enrichments during the merging of these different phases caused the dimples to form on the particle surface (Vehring, 2007).

3.2. Morphology of microcomposites after heat treatment

After calcination, iron oxide crystals appeared on the surface of the particles. The SEM observations are shown in Figs. 3 and 4. The crystals were typically iron oxide, as confirmed by XRD observation (Fig. 5). Different calcination
The appearance of crystals after heat treatment can be explained by the chemistry of iron oxide formation (Jolivet et al., 2004). Ferrhydrite had a good dissolution with delayed phase transformation with addition of ligands (Doelsch et al., 2000; Jolivet et al., 2004; Farfitt et al., 1992), which were Cl⁻ in this case. The initial formation of β-FeOOH was caused by the presence of high content of Cl⁻ as anionic ligands with high affinity for the partly hydrolyzed iron. This type of ferrhydrite had a structure consisting of four double rows of FeO₃(OH)₃ octahedra to form a square tunnel linked by corner sharing and by weak hydrogen bonds. The part of the open tunnel was filled and stabilized with Cl⁻ ions, while the main structure was stabilized by a proportion of O₂⁻ instead of OH⁻. With continuing hydrolysis process, these Cl⁻ ions were gradually expelled and O₂⁻ started to attract H⁺ to form by OH⁻ ions to stabilize the molecular structure while the bonds forming the square structure broke to form the 6-line ferrhydrite (Fig. 6: reaction (i)) (Bottero et al., 1994; Jolivet et al., 2004; Schwertmann et al., 1999). Olation reaction transformed metal ions to form polymeric oxides in aqueous solution (Fig. 6: reaction (ii)), while oxolation reaction was the opposite of olation process and was triggered by acetic acid so that the ionization and condensation processes could continue (Fig. 6: reaction (iii)). Normally, these reactions happened simultaneously to form hematite (Fig. 6: reaction (iv)). At a low concentration of chloride, 6-line ferrhydrite (the empirical formula of which was still debated between Fe₃H₀₄·4H₂O, Fe₂O₃Cl, or Fe₃O₄·2FeOOH·2.6H₂O), would form initially and transform into hematite during heat treatment. With the presence of inert environment during calcination, this hematite could be transformed into magnetite according to reaction shown in Fig. 6: reaction (v) (Cornell and Schwertmann, 1996; Jambor and Dutrizac, 1998; Jolivet, 2000; Jolivet et al., 2004; Matthews, 1976; Mucke and Cabral, 2005; Schwertmann et al., 1999). However, no magnetite peaks could be clearly distinguished via XRD (Fig. 5) in this case, possibly due to the low crystallinity of the iron oxide formed.

The main difference between these FCA recipes was the amount of silica nanoparticles being added into the mixture, while the pH of the initial precursors was similar. With higher amount of silica nano-particles, the shell was more packed and comprised mainly of these nano-particles (Iskandar et al., 2001; Wang et al., 2007). With less iron component present on the particle shell, there would be less opportunity to grow larger crystals on the shell. In contrast, calcined FCA2 samples showed a chain of crystals on the surface (Fig. 4). A few larger crystals were observed, mostly with cubical shapes. There were no colloidal particles as constituents in the precursors for FCA2. With no silica nano-particles, the shell of FCA2 samples was formed only by a combination of lactose and iron. Thus there would be more iron available on the particle surface, with the possibility of surface water layer saturated with iron ions, to form more crystals. Subsequent aggregation of these crystals could create the chain-like morphology, covering the particle surface or continue to grow into larger crystals.

3.3. Magnetism properties

Fig. 7 shows that the magnetism values for FCA1 and FCA2 increased with longer calcinations period. This condition can be explained from the chemistry of iron oxide crystal formation as discussed in the previous section. FCA precursors utilised acid to dissolve the iron salts, so β-FeOOH would be formed as the starting point for crystal formation (Jolivet et al., 2004). Due to the initial formation of β-FeOOH, the calculation time required for crystal formation and growth would be

(i) Initial precipitates formation:

\[ \text{Fe}(\text{H}_2\text{O})_3^{3+} \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_3\text{OH}]^{2+} + \text{H}^+ \]

(ii) Olation reaction:

\[ [\text{Fe}(\text{H}_2\text{O})_3\text{OH}]^{2+} + [\text{Fe}(\text{H}_2\text{O})_3]\rightarrow [\text{Fe}(\text{H}_2\text{O})_3\text{H}]^{2+} + \text{H}_2\text{O} \]

(iii) Oxolation reaction:

\[ [[\text{Fe}(\text{H}_2\text{O})_3\text{H}]^{2+} + \text{H}^+ \rightarrow [[\text{Fe}(\text{H}_2\text{O})_3\text{H}]]^{2+} + \text{H}_2\text{O} \]

(iv) Total reaction:

\[ 2[\text{Fe}(\text{H}_2\text{O})_3]\rightarrow 2\text{Fe}_3\text{O}_4 + 6\text{H}_2\text{O} + 6\text{H}^+ \]

(v) Formation of magnetite from hematite:

\[ 3\text{Fe}_3\text{O}_4 + 2\text{H}^+ \rightarrow 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \]
longer. Thus the magnetism value was still increasing with longer calcination time, as shown in VSM data (Fig. 7).

Between the two batches, the relative values of magnetisation were relatively higher in FCA2, which had no silica nanoparticles in the precursor mixture (Fig. 7 and Table 1). This could be due to the tendency of silica nanoparticles to position themselves on the outer shell of the particles (Iskandar et al., 2001; Wang et al., 2007). Without silica nanoparticles, the shell of the particles in FCA2 had larger crystal size (Fig. 4) providing stronger magnetism, without the added presence of non-magnetic silica on the microcomposites.

4. Conclusions

The use of microfluidic spray drying to generate uniform magnetic microcomposites was demonstrated, specifically focusing on the effects of precursor composition, droplet size, and post-drying heat treatment on the final properties of the particles. The addition of silica nanoparticles in the precursor was shown to produce bowl-like particles, while spherical particles with dimpled surfaces could be generated in the absence of silica. These particles had higher magnetic strength after calcination, due to the presence of larger and more iron oxide crystals on the surface. Calcination period was shown to affect the magnetisation of the microcomposites, with increasing strength observed at longer periods. As the initial solutions were prepared in acidic condition, the formation of β-FeOOH in the precursors that was later converted into 6-line ferrhydrite would be the starting point in the reactions to form the iron oxide crystals on the particle shells.

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References


