

The effect of mixing on silver particle morphology in flow synthesis

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HIGHLIGHTS

- The mixing effects on the morphologies of silver particles were firstly investigated.
- Silver particles with controllable shapes were synthesized by continuous experiments in a T-mixer.
- With mixing intensity rising, the silver particles switched from plates to dendrites.
- Highly complex particle structures were characterized by analytical centrifugation and Brownian Dynamics simulations.
- Mixing-dependent particle growth modes were proposed in this paper.

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ABSTRACT

Silver particles, prepared in a T-mixer under different flow rates, were selected to study the influences of mixing on particle shape evolution. Mixing effects on particle growth were visualized by scanning electron microscopy (SEM) and analysed quantitatively by sedimentation coefficient distributions derived from analytical centrifugation (AC). The mixing time under different flow rates was determined by the Villermaux-Dushman method to quantify the mixing quality. Based on the finding of a mixing-induced shape transformation from plates to dendrites, an extended growth mechanism involving mixing effects was proposed. Slow mixing leads to a non-uniform distributed reactant mixture and low effective supersaturation. This causes preferential growth of high-energy facets resulting in plate-like particles with broad, multimodal sedimentation distributions. In contrast, fast mixing, corresponding to uniform reactant mixture and thus high effective supersaturation and nucleation rate, leads to dendritic products, and narrow but bimodal sedimentation distributions.

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1. Introduction

The synthesis of particles with controlled sizes and shapes is an important topic in the field of materials science and particle technology. However, it is widely known that not only thermodynamic conditions but also kinetic processes have significant and manifold effects on the final products. In various systems, these kinetic

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processes are adjusted to achieve narrow particle size and shape distributions (Kwon and Hyeon, 2008; Tao et al., 2008; Wang et al., 2015), which are often required in applications.

Two universal kinetic factors, reaction and mass transfer play a key role in particle morphology evolution (Dirksen and Ring, 1991; Tai, 1997; Xiao et al., 1990). Witten et al. proposed two classic models: diffusion-limited aggregation (DLA) (Witten and Sander, 1981) and reaction-limited aggregation (RLA) (Ball et al., 1987). This motivated Grzybowski's team to use a reaction-diffusion strategy to explain and analyse the formation of various kinds of patterns (Grzybowski et al., 2005). On the basis of these findings, our team proposed the reaction-diffusion methodology as a strategy for controlling particle shapes. Along these lines, interesting shapes were observed, e.g. snowflake-like calcium carbonate particles were synthesized by a compromise of reaction and diffusion (Wang et al., 2013); reversible shape variation between silver

dendrites and polyhedrons was realized by designed competition between the complexation and reduction of silver ions (Liu et al., 2015); and the reaction-diffusion conditions during particle growth were quantified experimentally by the Damköhler number (Yang and Han, 2016).

Mixing as the inevitable procedure bringing the reactants into contact is the first step during particle synthesis and thus can greatly affect the course of particle formation (Bałdyga and Bourne, 1999; Gradl and Peukert, 2010; Metzger and Kind, 2016; Schwarzer and Peukert, 2004). Although in our previous works (Yang and Han, 2016; Yang et al., 2015, 2017), the effects of monomers' microscopic mass transfer (i.e. diffusion) have been considered and discussed under the assumption of ideal mixing, the influence of mixing on the formation and evolution of particles with complex shape is still unknown. However, in particular, in a technical production process, beyond molecular diffusion, convective mass transfer is expected to play a significant role for particle formation. In the case of particle systems with fast formation kinetics, the mixing-dependent distribution of monomer concentration in time and space governs supersaturation, the thermodynamic driving force for phase transition. An incomplete chemical reaction due to poor mixing has a strong influence on both nucleation and growth of particles. Thus, mixing can become a decisive factor for the product quality (Meincke et al., 2017; Peukert et al., 2015), not only in terms of the width of a particle size distribution (PSD) (Fitchett and Tarbell, 1990; Yu, Shekunov et al., 2001; Zauner and Jones, 2000) but also in terms of the final particle shape.

To address this important issue, we used silver nanoparticles as the technically relevant model system with promising applications in biology (Abbasi et al., 2016; Yoon et al., 2008), optics (Klupp Taylor et al., 2010; Sathyavathi et al., 2010), and catalysis (Baruah et al., 2013). To unravel the effects of mixing on particle shape evolution, scanning electron microscopy (SEM) and analytical centrifugation (AC) were used to study the morphologies and sedimentation properties of the particles, respectively. In particular, AC turned out to be the method of choice for the characterization of complex particles as it allows taking into account all particles of a sample and not only snapshots of the representative species. First, the influence of mixing modes was tested by batch experiments to get an overview whether or not mixing has an effect on the shape evolution. Then, controlled mixing conditions were realized by continuous experiments in a T-mixer under different flow rates. Particles were characterized by SEM and AC, and the particles' morphology was linked to the sedimentation coefficient distributions supported by Brownian Dynamics (BD) simulations. For all experimental settings, the mixing quality was quantified by previously determined mixing time using the Villiermaux-Dushman protocol (Commence and Falk, 2011; Guichardon and Falk, 2000; Guichardon et al., 2000). Via this way, correlations between mixing intensity and particle size and shape distributions could be derived. Although many studies on the influence of mixing on spherical particles do exist (Metzger and Kind; Thajudeen

et al., 2017; Walter and Peukert, 2016), the impact of mixing on the evolution of highly complex structures, i.e. in our case from sheet-like to dendritic products, has not yet been demonstrated. On the basis of these findings, the reaction-diffusion mechanism from our previous works was extended for mixing effects.

2. Experimental section

2.1. Chemicals and equipments

Silver nitrate (AgNO_3 , 99.9999% trace metals basis) and hydroxylamine (NH_2OH , 50 wt% aqueous solution) were purchased from Sigma-Aldrich. Ethanol (absolute) was provided by VWR. Sulphuric acid (H_2SO_4 , 96%), sodium hydroxide (NaOH , $\geq 99\%$), potassium iodide (KI , $\geq 99.5\%$), potassium iodate (KIO_3 , $\geq 99.5\%$), boric acid (H_3BO_3 , $\geq 99.8\%$) and ethylene glycol (EG, 99.5%) were bought from Carl Roth. All chemicals were used without further purification. Deionized water from a Millipore (MQ) system had a resistivity higher than $18 \text{ M}\Omega \text{ cm}$ throughout all our studies. Flasks (100 mL) and disposable syringes (50 mL) were obtained from VWR and Carl Roth, respectively. The one-channel syringe pumps (NE-800) were products of New Era Pump Systems, Inc. All experiments were conducted at room temperature. 0.1 M AgNO_3 and $0.2 \text{ M NH}_2\text{OH}$ stock solutions were prepared by dissolving silver nitrate and diluting hydroxylamine in Millipore water.

2.2. Definition of experiment types

As illustrated in Fig. 1, four types of mixing were defined, three (M0, MA, MB) for batch experiments and one (MT) for the continuous experiments in the T-mixer. The total volume of the reactant mixture was kept constant at 50 mL throughout all experiments and the final equivalent concentrations of silver nitrate and hydroxylamine in the reactant mixture were maintained as 1 mM and 2 mM, respectively. Batch experiments were carried out in a 100 mL round-bottom flask under 200 rpm stirring by a typical magnetic lab stirrer bar with an oval shape and 20 mm length. The continuous mixing experiments were conducted in a T-mixer, and were realized by two syringe pumps. The upper limitation of the flow rate for the pump equipped with a 50 mL syringe is $201.1 \text{ mL min}^{-1}$. The underlying experimental procedures are described in the following.

M0. M0, taking the same procedure as that in the previous paper (Yang et al., 2015), was implemented by first mixing 49 mL of water and 0.5 mL of AgNO_3 stock solution, and then adding 0.5 mL of NH_2OH stock solution by a pipette under vigorous stirring.

MA. For MA, 0.5 mL AgNO_3 and 0.5 mL NH_2OH stock solutions were separately mixed with 24.5 mL of water, and then the diluted NH_2OH solution was quickly poured into the AgNO_3 solution under vigorous stirring.

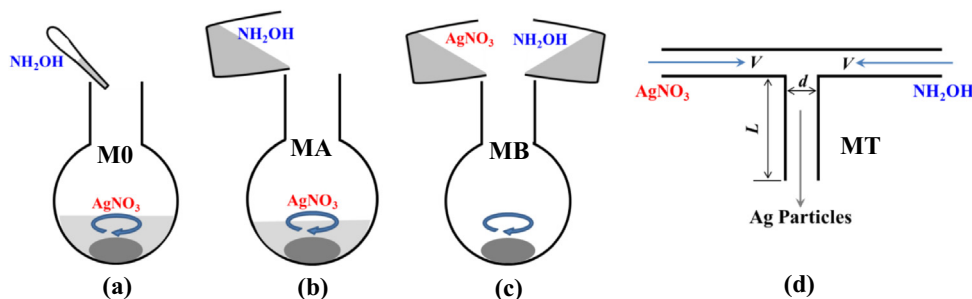


Fig. 1. Four different mixing modes for the preparation of silver particles. The first three (a-M0, b-MA, c-MB) are batch experiments and the last one (d-MT) corresponds to the continuous setup.

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