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# Growth of Nanoparticles and Microparticles by Controlled Reaction-Diffusion Processes

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**ABSTRACT:** The synthesis of different sizes of nanoparticles and microparticles is important in designing nanostructured materials with various properties. Wet synthesis methods lack the flexibility to create various sizes of particles (particle libraries) using fixed conditions without the repetition of the steps in the method with a new set of parameters. Here, we report a synthesis method based on nucleation and particle growth in the wake of a moving chemical front in a gel matrix. The process yields well-separated regions (bands) filled with nearly monodisperse nanoparticles and microparticles, with the size of the particles varying from band to band in a predictable way. The origin of the effect is due to an interplay of a precipitation reaction of the reagents and their diffusion that is controlled in space and time by the moving chemical front. The method represents a new approach



and a promising tool for the fast and competitive synthesis of various sizes of colloidal particles.

## 1. INTRODUCTION

The synthesis of nanoparticles and microparticles (NPs, MPs) of controlled size and shape has gained importance during the past few decades because of the application of such colloidal particles in chemistry, physics, materials science, and medicine.<sup>1-5</sup> There are two basic challenges in synthesis: the first is to synthesize particles with the desired size/shape, and the second is to reduce their polydispersity. The size and shape of particles typically affect their physical and chemical properties.<sup>6-15</sup> For example, the catalytic activity of the NPs depends on the particle size,  $^{11,12}$  and the toxicity of gold NPs is known to be size-dependent.  $^{6,13,14}$  The size of submicrometersized metal oxide particles can determine their photonic properties in water-splitting photoelectrodes.<sup>16</sup> Moreover, inherent polydispersity, which arises during synthesis, can modify the self-assembly, resulting in nanostructured materials,<sup>17</sup> thus affecting the overall characteristics of the sizedependent properties of individual NPs and MPs (e.g., their surface plasmon resonance<sup>18</sup> or magnetic susceptibility<sup>19</sup>). There are methods (e.g., synthesis using polymeric stabilizers or reverse micelles) in which a low degree of polydispersity can be achieved.<sup>20-22</sup> Particle synthesis combined with microfluidics provides a method for the synthesis of particles with different sizes and surface compositions (libraries of particles).<sup>23,24</sup> However, in most cases, the particles need to be purified after synthesis.<sup>25</sup> Furthermore, in all those methods using a given set of experimental (e.g., reaction) conditions and parameters provides just a given average size and shape of

particles. To obtain monodisperse particles of various sizes, the experimental conditions and parameters must be changed and the procedure should be repeated.<sup>26</sup> Moreover, for industrial applications, synthesis should be a low-cost and rapid process. The design of synthesis methods with fixed conditions and parameters that can provide particles sorted according to their size is rather challenging. Wet synthesis methods are based on redox reactions (e.g., synthesis of noble metal NPs from salt using reducing agents)<sup>27,28</sup> or precipitation reactions (e.g., synthesis of CdS NPs).<sup>29,30</sup> Here we show a novel approach for the synthesis of NPs and MPs using a bottom-up/self-assembly process in which particles with different sizes are spatially sorted into nearly monodisperse regions. The method is based on using initially separated reagents and controlling the nucleation and growth of particles by spatiotemporally varied diffusion fluxes.

To illustrate our concept, we chose a precipitation process with pattern formation (the classical Liesegang phenomenon) in reaction-diffusion systems.<sup>31</sup> In this emblematic example of self-organization, pattern formation occurs because of the interdiffusion and chemical reaction between two chemical compounds (the outer and inner electrolytes) resulting in distinct precipitation bands. It has been presented in a previous study that in a Liesegang system (cobalt oxinate) the average

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size of the formed millimeter-sized particles (the size of particles varied between 0.18 and 0.28 mm) increases with the band number.<sup>32</sup> As we shall see, these bands play the role of drawers where particles of a given size are collected. The experiments are carried out in hydrogels, which prevent both sedimentation of the colloids formed in the precipitation reaction and hydrodynamic instabilities that would otherwise destroy the spatial structures. The inner electrolyte is placed in a gel, and the outer electrolyte diffuses from a solution or another gel with a high initial concentration. Thus, pattern formation is driven by a diffusively moving chemical front.

#### 2. EXPERIMENTAL SECTION

We used the so-called wet stamping (WETS) method for the synthesis of particles (Figure 1a).<sup>33</sup> A solid hydrogel stamp introduces the



Figure 1. Sketch of the experimental setup using the wet stamping method (a). SEM micrograph of the spatial pattern consisting of quasiperiodic precipitation bands/rings (b). Band 1 emerged in the wake of the reaction front, followed by the consecutive formation of bands 2-9.

invading (outer) electrolyte into a thin gelatin film containing a coprecipitating (inner) electrolyte. When the stamp is placed on the film, the invading electrolyte diffuses into the gel and precipitate rings are formed around the location where the stamp came into contact with the film. The film thickness is approximately 1  $\mu$ m. The gelatin film (10 w%, Acros) containing the inner electrolyte (0.01 M  $K_2Cr_2O_7$ , Acros, extrapure 99.5%) and NH4OH (0.014 M, Acros) is produced by spin-coating the hot gelatin solution (65 °C) on a silicon wafer (700 rpm) that is than allowed to dry for 24 h at ambient temperature. The agarose stamp is made from an agarose solution (6 wt % OmniPur Agarose, Merck, prepared with degassed Milli-Q water) that is heated in a microwave oven and poured on a preshaped polydimethylsiloxane (PDMS) mask containing cylindrical features of 500  $\mu$ m in diameter with the distance between features being 1 mm. The degassed and cooled agarose block is removed from the mask, cut into 0.4 cm  $\times$  0.4 cm pieces (3 pins  $\times$  3 pins), and soaked in AgNO<sub>3</sub> solution (0.3 M, Acros, extra pure 99.85%). After 2 days, the soaked stamps are dried on a filter paper for 2 min and placed on the gelatin films for 2 h. After the agarose stamp was removed from the gelatin film, all samples were dried and sputter-coated with gold and examined with scanning electron microscopy (REM-FEI Nova Nano SEM 230).

The scanning electron micrographs, as shown in Figures 1 and 2, are our prime experimental data and allowed us to carry out particle size distribution analysis using digital image processing. The same holds for the quantitative analyses of the bands and rings.

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**Figure 2.** Fine structure of the bands (a) and the interband regions (b) presented in Figure 1b. Bands and the interband region contain nanoparticles and microparticles whose size varies with the position of the bands.

#### 3. RESULTS AND DISCUSSION

As the silver nitrate diffuses out of the stamp, the reaction between silver and dichromate ions results in a reaction product near the pins that transforms into a precipitate if the local concentration of the reaction product reaches a threshold concentration (Figure 1a). The precipitation process is fast compared to diffusion, and it depletes the inner electrolyte (potassium dichromate) near the zone lowering its local concentration. Therefore, the local concentration of the reacting product remains below the precipitation threshold, and a new separate band forms only at a distance from the existing band where this threshold is reached again. This process occurs repeatedly, creating numerous precipitation rings around the features of the stamp (Figure 1b). The process described above is known as Liesegang pattern formation or, more generally, quasiperiodic precipitation.<sup>31,34</sup> We investigated the structure of the Liesegang bands and found that the zones contain particles as observed in earlier experiments,<sup>32</sup> and the average particle size increases with distance from the junction point of the electrolytes (Figure 2a). Interestingly, we found particles in between the bands as well. Their density is much lower, and they are much smaller than the particles in the bands, with their sizes in the first zones being smaller than 100 nm (Figure 2b).

From a technological point of view it is important to know and understand the dependence of the average size of particles on material parameters. To derive this dependence theoretically, we consider the Liesegang dynamics after the *n*th band has formed.<sup>35,36</sup> Liesegang dynamics includes a diffusion front of the outer electrolyte and a reaction between the outer and inner electrolytes according to the reaction  $A + B \rightarrow C$ , where A, B, and C denote the outer electrolyte, the inner electrolyte, and the reaction product, respectively. This reaction product can further turn into a precipitate.<sup>35–37</sup> As shown in Figure 3, the diffusion front  $x_f(t) = (2D_f t)^{1/2}$  is past the *n*th band ( $x_f > x_n$ and  $D_f$  is the diffusion coefficient of the front, which depends on the diffusion coefficients and on the initial concentration of



**Figure 3.** Profile of the concentration of the reaction product, *C*, (c(x, t)), green line) near the front position  $x_f(t) > x_n$  once the *n*th band has been formed and the (n + 1)th band is about to form. The concentrations of the reagents, a(x, t) and b(x, t), are shown in red and blue, respectively, with their asymptotic values given by  $a_0$  and  $b_0$ . The spinodal concentration  $c_s$  for the reaction product is shown by the dotted line. The incoming flux of the reagents to the front and the outgoing flux of the reaction product are calculated by assuming linear concentration profiles in the vicinity of the reaction zone.

the electrolytes). The concentration of the reaction product (C) that will turn into the precipitated particles at  $x_f(t)$  is maximal, and  $c_{max}(t)$  increases as the front moves farther away from the band. As  $c_{max}(t)$  approaches the spinodal value  $c_{s'}$  the rate of formation of the nucleation centers increases. The nucleation centers deplete the reaction product within a radius of  $(2D_c\delta t)^{1/2}$ , where  $\delta t$  is the time after the nucleation started, so that no new centers form once the depleted regions fill the space. Using the above picture, we can determine the size of the particles as follows. Let the number of centers in a volume V be  $N_c$ . Then the average distance l between the centers can be calculated as

$$l = \left(\frac{V}{N_{\rm c}}\right)^{1/3} \tag{1}$$

and if we recall now that a constant concentration of reaction product (C) is left behind the front  $(c_0)$ ,<sup>36</sup> then eq 1 gives the radius of the particles  $r_p$  through the equality

$$c_0 V = N_c c_p \frac{4\pi}{3} r_p^{\ 3} \tag{2}$$

where  $c_p$  is the concentration of the reaction product in the particles, which we assume to be a constant and independent of the band number. Thus

$$r_{\rm p} = \left(\frac{3c_0 V}{4\pi c_{\rm p} N_{\rm c}}\right)^{1/3} = l \left(\frac{3c_0}{4\pi c_{\rm p}}\right)^{1/3} \sim l$$
(3)

and the time-evolution of l(t) determines the time evolution of  $r_{p}(t)$ .

An estimate for l(t) is given by

$$l = \sqrt{2D_{\rm c}\,\delta t} \tag{4}$$

thus the task is to estimate the time available for the centers of nucleation to collect reaction product C before the depleted regions start to overlap.

To calculate  $\delta t$ , we assume that we are in the asymptotic regime of band formation, i.e., the band number *n* is large and the front moves slowly. Accordingly, the maximum value of the

concentration of the reaction product grows slowly in the front region (Figure 3). We can see this by calculating  $c_{\max}(t)$  from the condition that the incoming flux,  $j_{in}$ , of reagent A is equal to that,  $j_{out}$ , of reaction product C leaving the front region (Figure 3)

$$D_{\rm a} \frac{a_0}{x_{\rm f}(t)} = D_{\rm f} \frac{c_{\rm max}(t)}{x_{\rm f}(t) - x_{\rm h}}$$
(5)

yielding

$$c_{\max}(t) = \frac{D_{a}a_{0}}{D_{c}} \left(1 - \frac{x_{n}}{x_{f}(t)}\right) = \frac{D_{a}a_{0}}{D_{c}} \left(1 - \frac{x_{n}}{\sqrt{2D_{f}t}}\right)$$
(6)

where  $D_{\rm a}$  is the diffusion coefficient of reagent A and  $a_0$  denotes the concentration of A at the gelatin–agarose stamp interface (placed at the origin). We can see now that  $c_{\rm max}(t)$  indeed increases slowly at long times because  $\dot{c}_{\rm max}(t) \approx t^{-3/2}$ .

Nucleation mainly occurs in the  $c \approx c_{\text{max}}$  region. Let us assume that there is a lower limit  $c \approx c_1$  where the nucleation rate is still small but starts to be appreciable, i.e., the number of nucleation centers formed per unit time is given by

$$R_1 = Q_0 e^{-\beta \delta F(c_1)} V \tag{7}$$

where  $F(c_1)$  is the free-energy barrier to nucleation at a  $c_1$  concentration of particles C,  $\beta$  is the inverse temperature, V is the volume of the system, and  $Q_0$  is some unknown amplitude related to the time scale. We also have an upper value  $c \approx c_2$  where the nucleation becomes fast and all of the regions that have not been depleted are quickly filled with centers of nucleation (this will happen the latest when reaching the spinodal,  $c \approx c_s$ ).

We shall assume that the nucleation centers formed in the initial stages determine the large particles and the distance between them. They are depleting a region around themselves that has a radius of  $(2D_c\delta t)^{1/2}$ , where  $\delta t$  is the time the system requires to evolve from  $c_1$  to  $c_2$ . Because this radius gives us  $l(t) = (2D_c\delta t)^{1/2}$ , all we have to do is calculate  $\delta t$ .

To obtain  $\delta t$ , we need to calculate the times t and  $t + \delta t$  when the maximum concentrations of the reaction product reach the values  $c_1$  and  $c_2$ ; i.e., using eq 6 we need to solve the following two equations

$$c_1 = \frac{D_a a_0}{D_c} \left( 1 - \frac{x_n}{\sqrt{2D_f t}} \right) \tag{8}$$

$$c_{2} = \frac{D_{a}a_{0}}{D_{c}} \left( 1 - \frac{x_{n}}{\sqrt{2D_{f}(t+\delta t)}} \right)$$
(9)

Because we are in the asymptotic regime, we can expand the second equation to obtain

$$c_{2} = \frac{D_{a}a_{0}}{D_{c}} \left( 1 - \frac{x_{n}}{\sqrt{2D_{f}(t+\delta t)}} \right) = c_{1} + \frac{D_{a}a_{0}}{D_{c}} \frac{x_{n}}{\sqrt{2D_{f}t}} \frac{\delta t}{t}$$
(10)

Using now the above formulas when the (n + 1)th band is forming, i.e.,  $t \approx t_{n+1}$  and  $(2D_{t}t_{n+1})^{1/2} = x_{n+1}$ , we can write

$$c_2 - c_1 = \frac{D_a a_0}{D_c} \frac{x_n}{x_{n+1}} \frac{\delta t}{2t_{n+1}}$$
(11)

Because  $x_n/x_{n+1} = 1/(1 + p)$ , where *p*, the so-called spacing coefficient,<sup>33,36</sup> is constant, we can further simplify to obtain the final expression

$$\delta t = \frac{2(c_2 - c_1)D_c(1+p)}{D_a a_0} t_{n+1}$$
(12)

Substituting the result for  $\delta t$  into the expression for l(t) (eq 4), we obtain

$$l = \sqrt{2D_{c}\delta t} = \sqrt{2D_{c}\frac{2(c_{2} - c_{1})D_{c}(1 + p)}{D_{a}a_{0}}}t_{n+1} \sim \sqrt{2D_{c}t_{n+1}} \approx x_{n}$$
(13)

Thus, we have the following result. The distance between the large particles in the *n*th band is proportional to  $x_n$ . Using eq 3, we find that the radius of a particle is

$$r_{\rm p} \sim l \sim x_n \tag{14}$$

We have arrived at the main theoretical result of our work. Namely, we found that there is a linear correlation between the size of the particles and the position of the band measured from the gelatin—agarose stamp interface.

The nontrivial result of the above calculations is that, because of the general diffusive scaling present in the dynamics of the formation of the Liesegang bands, one finds that the  $\delta t \sim t_n$ which can be interpreted as if the particles had the time  $t_n$  for growth. This is why one can make contact with experiments on crystal growth where the size of the crystals satisfies the wellknown time–size relationship  $r \sim t^{1/2}$  similarly to our case (eq 14).<sup>38</sup> Figure 4 shows the experimental results for particle



**Figure 4.** Variation of the diameter of particles in the bands (red symbols, bands were defined as indicated by red boxes in Figure 2) and between the bands (blue symbols) as a function of their distance from the junction point of the electrolytes. The size of the particles was determined using digital image analysis (ImageJ) software. The band numbers are as indicated in Figure 1

diameter in the precipitation bands and in between the bands. The trend is the same for both cases, and the size of the particles scales linearly with the distance of the band measured from the junction of the electrolytes. The size of particles in the interband region is much smaller than in the bands. Our theory does not take into account large fluctuations or the presence of impurities and consequently predicts no nucleation events in the interband regions, and we have no estimates for the size of the particles there. We note that the size of the particles in the interband region close to the agarose pin is lower than 100 nm. Improving the resolution of the bands near the pins may actually uncover even smaller particles.

The agreement between theory and experiment suggests that the nucleation rate at a given position can be obtained from the time evolution of the local concentration of the reaction product (C),  $c_{max}$ . Because the dynamics is determined by the front, its velocity is one of the main factors governing the number of nuclei per volume unit that can act as nucleation centers. Those nuclei can grow, and their growth rate and final size are predominantly driven by the rate of formation of the reaction product and its influx from the neighborhood. The above picture also suggests that the nucleation and particle growth can be controlled by the fluxes of the outer electrolyte and the reaction product through the local velocity of the diffusion front. Because the fluxes strongly depend on the position of the reaction front, controlling these fluxes either spatially or temporally can provide flexible control in the design of NPs and MPs.

An important issue is the polydispersity (the standard deviation of the size) of the particles. This varies with distance and is significantly smaller in the interband region. The latter is less than 10% for the interband particles, which is comparable to the polydispersity obtained from other liquid-phase synthetic methods.<sup>26</sup> Figure 5 shows in detail the probability distribution for the size of particles in the precipitation bands. The basis for the analysis was the SEM micrographs shown in Figure 2. It can be seen that the average size is shifted toward larger sizes and the distribution is broadened.

We have also studied the average particle size and its standard deviation in a cross section of a band (in the direction of the diffusion flux of the outer electrolyte, silver nitrate), and the results are presented in Figure 6. Similarly, we analyzed particles from Figure 2. The size distribution is symmetric, and the variation is more pronounced for large-order bands. In the first band, almost monodisperse MPs are formed, but they become more polydisperse with increasing band number. Near the edges of the bands the particles are smaller than particles in the center. This finding is consistent with our earlier discussion. Indeed, near the junction point of the electrolytes the front moves fast because of the high concentration gradient of the outer electrolyte. This ensures the same nucleation and growth rates in a spatially narrow region, thus resulting in the formation of the nearly monodisperse particles near the stamp interface. Farther from the interface, the degree of homogeneity of the nucleation zone is lessened by the slower motion of the reaction front and the increased width of the front.<sup>39</sup> This leads to inhomogeneities both in the rate of the emergence of the reaction product and in the rate of growth of particles, which in turn may be the reason for the polydispersity observed in the experiments with large band order. To have a more sophisticated picture of the morphology of particles, we used a 3D dual-beam scanning electron microscope (SEM-FIB: SEM-FEI Helios Nano Lab 650). These additional investigations verified that the particles have a basically spherical shape (Figure 7).

In our method, the diffusion of chemicals plays a crucial role. Thus, from a practical point of view, the effectivity and speed of the process may be questioned because mass transport by diffusion is usually considered to be a slow process. It is indeed a problem on the macroscale because the characteristic diffusion length (diffusion distance,  $x_{cr}$ ) is related to the characteristic diffusion time  $(t_{cr})$  through  $x_{cr} = (2Dt_{cr})^{1/2}$ , where D is the diffusion constant of the diffusive species. On the macroscale (a few centimeters range) and for small hydrated ions in water ( $D = 10^{-9} \text{ m}^2/\text{s}$ ), the characteristic diffusion time





Figure 5. Particle size distributions in the bands. Bands are defined as indicated by red boxes in Figure 2a. Red lines correspond to the fitted Gaussian curves.



**Figure 6.** Size of particles in the cross sections of bands (in the direction of the diffusion flux of the outer electrolyte). The distance (y) is measured from the centerline of the bands (yellow line in Figure 2a).



Figure 7. Cross section of a precipitation band using a 3D dual-beam scanning electron microscope (SEM-FIB: SEM-FEI Helios Nano Lab 650).

obtained from the above relation is on the order of a day. However, in our setup, where the characteristic diffusion length (the half distance between pins) is several hundred micrometers, the characteristic diffusion time is on the order of minutes. Therefore, the time is not a limiting factor.

#### 4. CONCLUSIONS

We have demonstrated a concept for a competitive, fast, lowcost method for the synthesis of NPs and MPs. In this bottomup approach, the different sizes of NPs and MPs are selfassembled into spatially well-separated domains (bands or regions between the bands) with controllable and predictable particle size. There are several factors that affect the particle size, e.g., the temperature, the initial concentrations of reagents, the thickness, and the chemical composition of the gel film, thus changing the experimental setup, and parameters can provide an easy way to control the size ranges of NPs and MPs. This method of engineering various sizes of NPs and MPs in one setup could provide a promising and versatile tool for material science. An obvious next step would be to apply this idea to the synthesis of NPs and MPs based on a redox reaction<sup>40</sup> in which a metal salt and reducing agents could be spatially separated, and the spatiotemporal variation of the local concentration and of the fluxes of the reagents would control the particle size and/or shape.

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#### Notes

The authors declare no competing financial interest.

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