

Material synthesis in non-equilibrium conditions

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Motivation

Chemical precipitation carried out under out-of-equilibrium conditions is a promising tool for producing solid materials. In this project, we have conducted experiments where spatial concentration gradients lead to the production of materials not accessible via commercial synthesis methods. In addition, the experiments have been supported by theory to acquire a deeper understanding of the system and hence achieve better control.

Based on the working packages we have summarized the main results in the following six points:

1 Macroscale patterns in 2D radial reactors as ground reference

Flow-driven precipitation with radial injection has been shown to follow various scaling laws such as power-law dependence of production rate and width on flow rate and height. We have designed a setup with a complexation reaction between iron(III) and thiocyanate ions where potassium thiocyanate solution is injected into a thin layer of the ferric nitrate solution resulting in a front in the form of a brown ring.⁷ The expansion of the ring (see Fig. 1) and the changes in its corresponding width are monitored

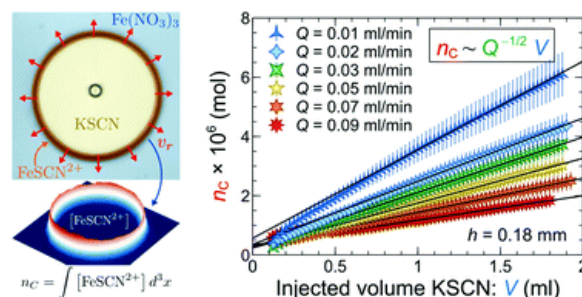


Figure 1: Spatiotemporal evolution of ferric thiocyanate complex.⁷

with imaging system in various configurations. We have shown that the amount of the product scales with the injection rate as the theoretical prediction if the solution height is sufficiently small. The temporal evolution of the front width also follows a power law with an exponent varying with both the injection rate and the solution height in disagreement of the theoretical prediction. This deviation is probably because of buoyancy and dispersion effects. The contribution of them can be deciphered under microgravity conditions. As a first step, a parabolic flight campaign, a prerequisite for sounding rocket missions, was completed in the fall of 2020. The sounding rocket flight as a TEXUS 57 mission is planned for early 2022.

2 Flow-driven precipitation in microfluidic reactors

We have used microfluidic reactors to synthesize lithium precipitates¹² and calcium oxalate.¹¹ Solutions of lithium chloride and sodium phosphate are injected simultaneously into the microchannel where precipitation reaction takes place along the contact line. The growth kinetics of individual precipitate particles is studied by monitoring the particle growth along and transverse to the flow. The growth rate parallel to the flow is independent of the injection rate, while transverse to it diffusion is the major driving force. The experimental findings were corroborated by modeling studies not only for lithium phosphate precipitates but also for a more complex system of calcium oxalate where we have shown numerically that the growth of calcium oxalate monohydrate is initially surface-limited. Furthermore, we have shown that the growth rate of individual particles is significantly slower in a crowded population and the particle size for particles leaving the channel monodisperse with

diameters about $2\ \mu\text{m}$.

3 Macro- and microstructure of flow-driven pattern formation in 3D spatial reactors

We have demonstrated the growth of hollow-tubed lithium phosphate hydrothermal vent-like precipitate structure. By injecting sodium phosphate solution into lithium chloride solution, a liquid jet appears, on which precipitate continuously builds upward with a linear growth rate independent of the injection rate until a maximum height is reached. Then the vertical growth stops while the tube diameter still increases. The analysis of growth profiles has revealed a linear volume growth rate with respect to the injection rate. The expansion in diameter, localized at the tip of the structure, scales with a power law suggesting that the phenomenon is controlled by diffusion and convection. (A manuscript summarizing the results is in preparation.)

We have shown that soft organic chemical gardens of chitosan hydrogel can develop upon injecting an acidic chitosan solution into an alkaline solution.¹⁴ Besides complex and budding structures, tubular hydrogel formations are also observed as illustrated in Fig. 2. Our finding proposes that organic garden can be observed in simple binary systems in the absence of metallic ions without classical precipitation reactions. Various types of surface instabilities can develop when the expanding hydrogel is constantly exposed to a rigid wall: Spontaneous symmetry breaking results in wrinkle-to-fold transition near the tip and wrinkling far from the tip. The wavelength of folds and wrinkles evolving during the boundary-aided growth shows linear scaling with the tube depth.¹⁶ The concentration gradient between the injected and the outer liquid drives the sol-gel transition with temporal scaling revealing diffusion as the main mode of transport across the interface under laminar flow conditions.

The properties of the *in situ* prepared membrane interface separating the alkaline and the acidic chitosan solution are investigated in the presence of various metal salts added to the acidic chitosan side.¹⁷ Upon the addition of the alkaline metal salt, folding pattern appears with decreasing periodicity and no variation in the characteristic properties, like tube diameter and depth. In contrast, these parameters increase for the alkaline earth metal chlorides. Wrinkles form at lower and intermediate calcium chloride concentration, while at high concentrations Liesegang-like concentric precipitations rings appear on a smaller length scale. These variations are the results of the increase in ionic strength that changes the gel properties by decreasing the repulsion between the polymer chains.

The membrane potential and the lifetime of the concentration cell formed is independent of the quality of alkali metal ions, but there is a slight dependence for alkaline earth cations. The calculated pH-driven potential

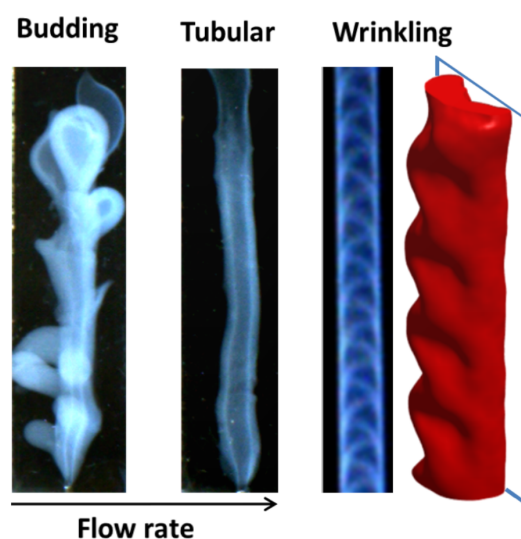


Figure 2: Flow-driven chitosan structures.¹⁴

difference is in good agreement with the experimentally measured one.

Local concentration gradients around a particle can generate active motion by converting chemical energy into mechanical. Numerous approaches have already been implemented to study the active motion under the influence of external stimuli and self-propulsion. We have developed a method where sol-gel transition-based paramagnetic beads are formed. This system opens the possibility to study the collective behaviors interacting through attractive and repulsive forces that mimic the emergent phenomena of biological systems like flocking of birds and swarming. We have identified the driving forces and characterized the dynamics of the system. The collective behavior significantly affected by the introduction of paramagnetic materials as ring ordering is observed when particles reach the lower energy state (see Fig. 3). A manuscript summarizing the results is in preparation.

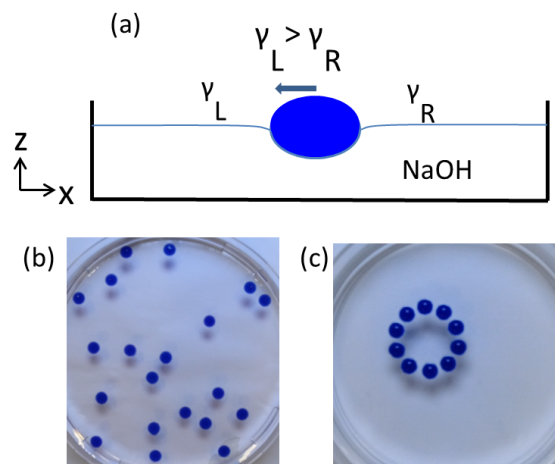


Figure 3: Self-propelled chitosan boat. (a). Spatial distribution of a flotilla in the absence (e) and in the presence (f) of paramagnetic material.

4 Self-assembly of oppositely charged nanoparticles

The application of the self-assembly of nanoscopic building blocks into higher-ordered structures plays a central role in chemistry, physics, and materials science with respect to the design and development of nanostructured materials with desired physical and chemical properties. In the framework of this research, we have extended the empirical law of the precipitation of oppositely charged nanoparticles (NPs), namely, oppositely charged NPs precipitate at the point of overall electroneutrality when the concentration of NPs exceeds a threshold concentration (precipitation threshold concentration, see Figure 4).^{1,2} We also proved that the solubility of an NP precipitate is dependent on temperature and that the dissolution process is irreversible. Similarly to the

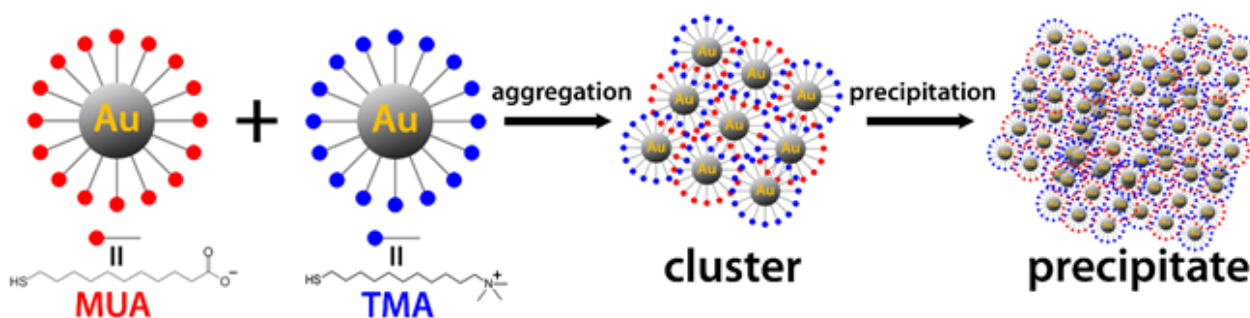


Figure 4: Schematic illustration of the precipitation process of oppositely charged nanoparticles; oppositely charged NPs form clusters that later coagulate to form a sediment consisting of microscopic aggregates.

solubility product of ionic systems, the precipitation threshold concentration may depend on the temperature, ionic strength, size of the NPs and chemical composition of the protecting NP monolayer. In addition to its technological relevance, this observation is fundamentally important because it shows that the precipitation processes of the charged building blocks of various sizes (ranging from ions to NPs) have a similar nature.

5 Control of the assembly processes of nanoparticles

We have developed two methods to drive and control of the self-assembly of various types of NPs. In the first technique, we used an alternative approach that focuses on a dispersion matrix, in which dispersed nanocrystals can be assembled into organized patterns by the non-uniform chemical reaction of the surrounding solvents.⁹ As a model nanocrystal, we employ silver nanowires (AgNWs) because they are one of the most important materials currently being explored in a broad range of applications. AgNWs were dispersed in a solution containing 2-hydroxyethyl methacrylate (HEMA) as a solvent. HEMA was polymerized via free-radical polymerization by light through a photomask, which modulated the intensity of the impinging light, and, in turn, generated lateral concentration gradients of the reactant (i.e., HEMA) and product (i.e., polymerized HEMA: PHEMA) over the mixture. Remarkably, such concentration gradients gave rise to the migration and organization of the AgNWs along the light patterns created by the photomask. The evolved AgNW structures were stable and embedded in the resultant PHEMA films on completion of the polymerization (see Figure 5). The prepared films exhibited favorable electrical conductivity and optical transparency, which depended largely on the light intensity distribution irradiated on the mixture during the reaction.

The second approach²¹ relies on a solvent evaporation, an aqueous L-(+)-tartaric acid (L-(+)-TA)/cellulose nanocrystals (CNC) mixture undergoes phase separation and subsequent precipitation, which being coupled with a diffusion-driven process, results in a rhythmic alternation of CNC-rich and CNC-depleted (or L-(+)-TA-rich) ring-type regions. The CNC-rich regions had a cholesteric structure with characteristic circular dichroism (CD) properties, while the L-(+)-TA-rich regions exhibited anisotropy stemming from radially aligned bundled structures (Figure 6). The moving front edge of the ring-banded pattern propagated with a finite constant velocity, which resulted in band periodicity controlled by film composition and evaporation rate. A proposed kinetic model qualitatively reproduced the experimental results. These results expand the range of self-organizing reaction-diffusion systems and pave the way for the design of periodically structured functional materials.

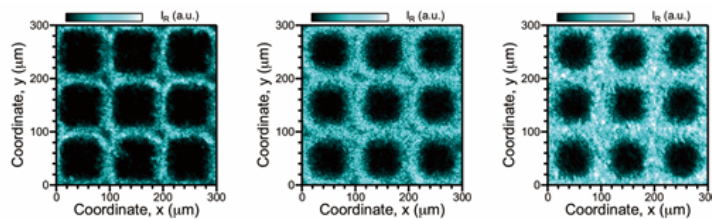


Figure 5: Self-assembly of AgNWs in the polymer matrix in which the polymerization was induced by irradiation.

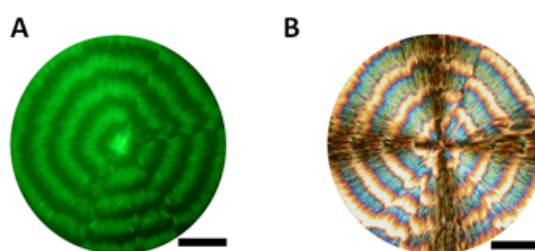


Figure 6: (A) Fluorescence microscopy and (B) polarized optical microscopy images of TA/CNC films. The scale bar is 100 μm .

6). The moving front edge of the ring-banded pattern propagated with a finite constant velocity, which resulted in band periodicity controlled by film composition and evaporation rate. A proposed kinetic model qualitatively reproduced the experimental results. These results expand the range of self-organizing reaction-diffusion systems and pave the way for the design of periodically structured functional materials.

6 Synthesis of gold nanoparticles by reaction-diffusion

The main aim of this project was to introduce a novel technique to generate gold NPs in a gelled medium. A solution of reducing agents (citrate) was put in contact with the gel containing gold salt (Au (III)). Upon diffusion of the reducing agent in the gel, a reaction-diffusion precipitation front invaded the gel leaving precipitate particles in its wake. Their size varies according to the local concentrations of reactants imposed by the diffusive flux. Synthesis by this method of colloidal particles with controlled size and shape has gained importance during the past decades due to their applications in chemistry, physics, materials sciences and medicine. We proposed to elaborate a gel method for the synthesis of gold NPs using a reduction process. Particles with different sizes and shapes spatially sorted into mono-disperse regions by controlling the nucleation and growth of particles via spatio-temporally varying diffusion fluxes (Figure 7). The effect of temperature, initial concentrations of reagents, thickness and chemical composition of the gel on the size ranges of particles were analyzed to set up a protocol for the controlled synthesis of nano- and microparticles in diffusive fluxes. Reaction processes (reduction, nucleation and particle growth) were modelled using a reaction-diffusion processes.

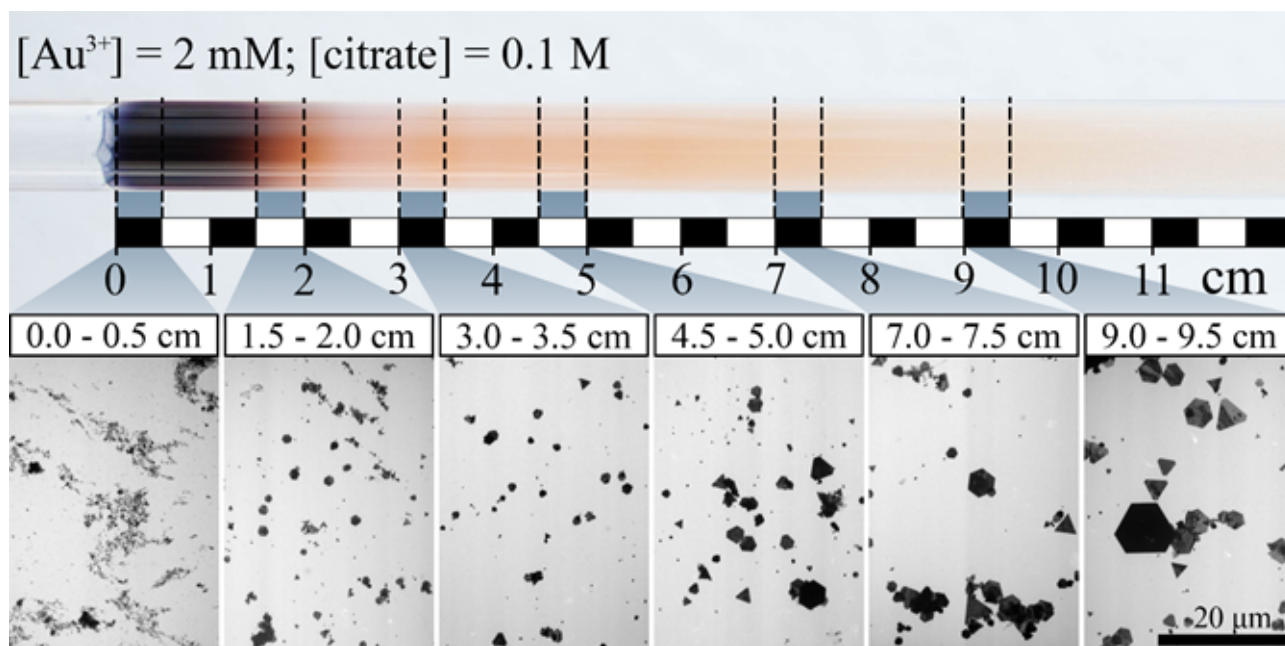


Figure 7: Synthesized gold NPs of various sizes and shapes in a reaction-diffusion process in an agarose hydrogel (0.1 m/v%) containing homogeneously distributed gold salt ($[\text{Au}^{3+}] = 2 \text{ mM}$), the citrate ($[\text{citrate}] = 0.1 \text{ M}$) diffused from outside (from the liquid phase placed on top of the gel column).

Summary

In short, we have successfully synthesized compounds ranging from nano- to microscale under out-of equilibrium conditions using flow in micro-, confined or 3D reactors and using diffusive flux in gels. Several techniques have been developed to produce bio-inspired or industrially relevant materials in a controlled manner. The experimental results are corroborated by modelling calculations including diffusion and advection.

Dissemination

We had a good start on strengthening the cooperation between participants with the first workshop organized by the Hungarian partners and held in BUTE in Budapest between January 23 and 26, 2019. We also met in Granada at a special 30/80 meeting where the results were presented in front of an international audience. The last fully personal meeting was held at the end of January 2020 in Prague. As a closing discussion, the members of the network participated in the COST Action hybrid meeting in Ankara in September 2021.

We have published 23 papers out of which 9 papers with master^{1,11,15,16} and doctoral^{7,8,12,20,21} students involvement and 3 students' work resulted in bachelor or master theses.²⁴⁻²⁶

Publications

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