

Final report

**Driven assembly at the nanoscale by nonlinear chemical
dynamics**

K104666

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István Lagzi

Budapest University of Technology and Economics

Abstract of the project proposal

Nowadays, the primary aim of nanoscience and nanotechnology is to synthesize particles and objects at nanoscale and to develop materials in that size. Nanoscale materials can be used in many useful and important applications e.g., in solar cells, energy storage, in industrial applications (using the catalytic property of the nanoparticles), in nanoelectronics or nanomedicine. The focus of nanoscience and nanotechnology is gradually shifting from the synthesis of individual components to their assembly into larger systems and use them as nanostructured materials. The primary goal of this project is to understand how nanoscience and nonlinear chemical dynamics can be used to drive assembly of nanoobjects. Based on this new "bottom-up" approach we will provide several applications where assembly of nanoparticles into ordered nanostructures will be driven by self-organizing chemical systems well-known at molecular level. Such nanostructures can have unique chemical and physical properties, therefore, they can be potential candidates in the future for several applications involving nanomaterials.

1. Self-assembly of colloids into helicoidal structure

In our works, we showed that emergence of helicoids and helices in precipitation processes in the wake of a planar reaction-diffusion front is an intrinsic property of the system and (in contrast to coming from initial and boundary condition effects) it can be attributed to the effect of the noise in the system. Our findings reveal that the emergence of helicoidal and helical patterns is reproducible with a finite, well-defined probability depending on the parameters of the system. We also investigated the microstructure (building blocks) of helical patterns, and we found that the precipitation helicoid consists of monodisperse spherulite-like particles of $\sim 1 \mu\text{m}$ size (Figure 1). These building blocks are achiral, and the macroscopic helicoids, which have four orders of magnitude larger size, emerged as a result of symmetry breaking, and not as a result of the microscopic chirality magnified to the macroscopic level.

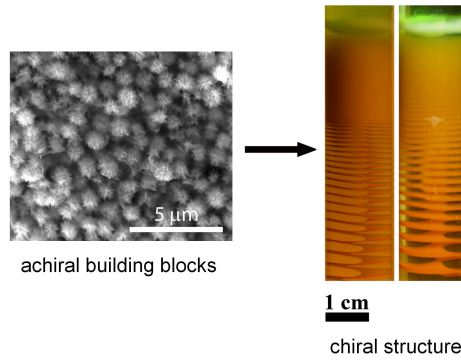


Figure 1 Helicoidal patterns in copper chloride/potassium chromate precipitation system.

In the framework of this project, we could understand the formation of these helicoidal structures. We developed a 3D reaction-diffusion model based on Cahn-Hilliard equation with a source term (ab) and noise (η_c) added

$$\partial_t a = \Delta a - ab ,$$

$$\partial_t b = \Delta b - ab ,$$

$$\partial_t m = -\lambda \Delta (m - m^3 + \sigma \Delta m) + ab + \eta_c(t) .$$

Here a and b are the concentration of the reagents, and m is the concentration of the precipitate. λ and σ are parameters of the Cahn-Hilliard equation. This equation features fast, spinodal-decomposition type dynamics, as well as slower, nucleation-and-growth processes. We applied

a time dependent noise (the amplitude of the noise is time dependent) in simulations and tested its effect on pattern stability. We found that the noise not only important for symmetry breaking at the beginning of the pattern evolution, but the noise stabilizes the existing helicoidal pattern.

Related papers:

- (i) S. Thomas, F. Molnár, Z. Rácz, I. Lagzi: *Matalon-Packter law for stretched helicoids formed in precipitation processes*, Chem. Phys. Lett., 577, 38-41, 2013
- (ii) S. Thomas, I. Lagzi, F. Molnár, Z. Rácz: *Probability of the emergence of helical precipitation patterns in the wake of reaction-diffusion fronts*, Phys. Rev. Lett., 078303, 2013
- (iii) S. Thomas, I. Lagzi, F. Molnár, Z. Rácz: *Helices in the wake of precipitation fronts*, Phys. Rev. E, 88, 022141, 2013
- (iv) S. Thomas, G. Varghese, D. Bardfalvy, Z. Racz, I. Lagzi: *Helicoidal precipitation patterns in silica and agarose gels*, Chem. Phys. Lett., 599, 159-162, 2014

2. Dynamic self-assembly of colloids into precipitation wave

Pattern formation in reaction-diffusion systems provides intriguing examples for the emergence of macroscopic order from molecular reaction events and Brownian motion. These patterns can be categorized as being spatially steady or unsteady and temporally static or dynamic. An extensively studied area of non-linear chemistry is the wave propagation in an excitable media. Belousov-Zhabotinsky (BZ) reaction provides a typical example to investigate several phenomena such as wave propagation and chemical chaos. Until now it has been accepted that there is no dynamic pattern formation in precipitation systems, and there are no similarities between patterns in excitable media and patterns emerging in precipitation reactions. This is because precipitation systems are simple, static, usually contain only two inorganic salts, and the formation of the precipitate is mainly dominated by local nucleation and growth processes. It is thereby hard to imagine that dynamic waves can exist in precipitation (heterogeneous) systems similar to those in excitable (homogeneous) systems. We showed that similar self-organized chemical waves can exist in several precipitation reaction-diffusion systems. The spontaneous appearance of traveling waves (spirals and target patterns) inside a thin and moving precipitation front in a hydrogel media is reported in aluminum hydroxide and mercuric iodide precipitation systems (Figure 2). A coexistence of moving precipitation layer with "excitable" traveling waves inside the precipitation layer is observed. Contrary to what is normally expected in waves propagating in other reaction-diffusion systems, these precipitation waves display superdiffusive behavior whereby the temporal evolution of the radius (R) of

propagating targets exhibits the power law $R \sim (time)$, with values of the exponent in the range of 0.65–0.84 depending on the initial concentrations of the reactants.

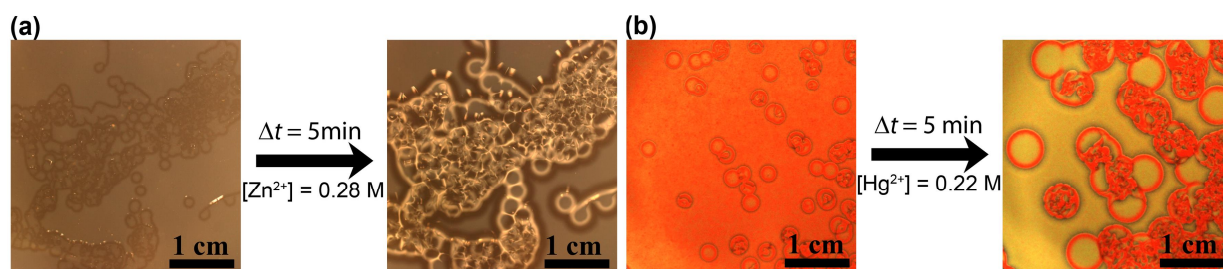


Figure 2 Chemical wave formation in (a) zinc hydroxide and (b) mercury (II) iodide systems in Petri dishes. The pattern formation was observed from the top.

Related papers:

- (i) B. Duzs, I. Lagzi, I. Szalai,: *Propagating Fronts and Morphological Instabilities in a Precipitation Reaction*, Langmuir, 30, 5460-5465, 2014
- (ii) M. M. Ayass, I. Lagzi, M. Al-Ghoul: *Three-dimensional superdiffusive chemical waves in a precipitation system*, Phys. Chem. Chem. Phys., 16, 24656-24660, 2014
- (iii) M. M. Ayass, M. Al-Ghoul, I. Lagzi: *Chemical Waves in Heterogeneous Media*, J. Phys. Chem. A, 118, 11678-11682, 2014
- (iv) M. M Ayass, I. Lagzi, M. Al-Ghoul: *Targets, ripples and spirals in a precipitation system with anomalous dispersion*, Phys. Chem. Chem. Phys., 17, 19806-19814, 2015

3. Synthesis and self-assembly of nanoparticles

We developed a novel, inexpensive and simple method to create a highly periodic, silver nanoparticle pattern using WET-Stamping technique. FIB-SEM studies demonstrated that the self-assembled bands are composed of ~160 nm diameter nanoparticles inside and on the surface of the gelatin film. Systematic analysis of the composition led us to two possible mechanisms for the formation of the bands starting from Ag₂O or Ag colloid particles. Subsequent thermal treatment at 360 °C removed the gelatin, turned any remaining Ag₂O to Ag and bound the silver particles to a conducting substrate, while the pattern is fully preserved. We believe this flexible and easily adaptable method will open up new possibilities for the preparation of meso- and nanoscale periodic silver structures for applications which include nonlinear optical components, antibacterial medical components, and transparent conducting grids on electrodes.

We have showed a simple concept to generate Voronoi diagrams using diffusion and aggregation processes of like-charged nanoparticles as building blocks by controlling the interactions between nanoparticles in a hydrogel (agarose, see Figure 3). The aggregation process of nanoparticles was triggered by the electrostatic screening of negatively charged carboxyl protecting groups by sodium ions. The coupling diffusion of nanoparticles and sodium ions and the aggregation of nanoparticles generate Voronoi diagrams, where the Voronoi cells consist of aggregated nanoparticles and their edges are aggregation-free and nanoparticle-free zones due to diffusion and fast aggregation processes. Our research provides an idea how to control spatiotemporally the self-assembly of nanoscopic building blocks by a diffusion front. Control of nanoscale systems by propagating reaction fronts could open up new avenues for research on nanostructured materials

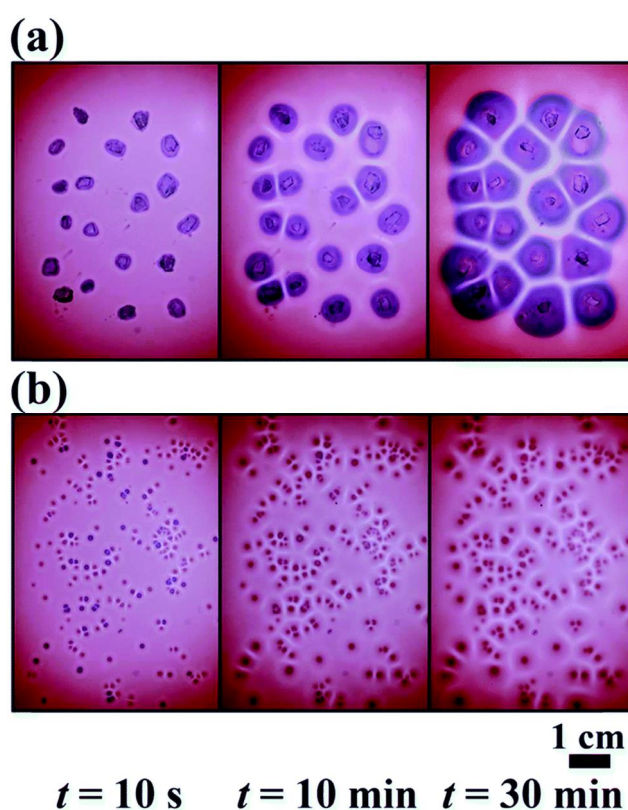


Figure 3 Formation of Voronoi diagrams in an agarose gel containing dispersed gold nanoparticles.

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. We provided a synthesis method based on nucleation and particle growth in the wake of a moving chemical front in a gel matrix (Figure 4). 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.

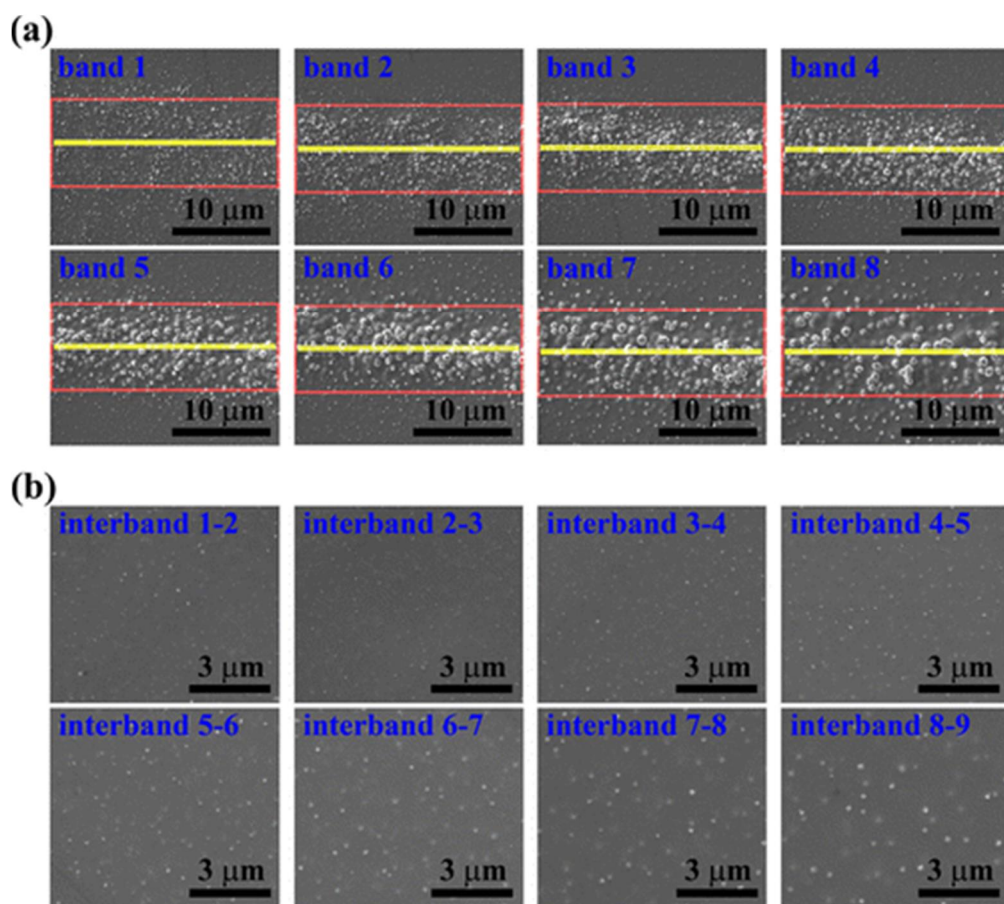


Figure 4 Fine structure of the bands (a) and the interband regions (b). Bands and the interband region contain nanoparticles and microparticles whose size varies with the position of the bands.

Related papers:

- (i) R Toth, RM Walliser, I Lagzi, F Boudoire, M Düggelein, A Braun, C E Housecroft, E C Constable: *Probing the mystery of Liesegang band formation: revealing the origin of self-organized dual-frequency micro and nanoparticle arrays*, Soft Matter, 12 (40), 8367-8374, 2016

- (ii) RM Walliser, R Tóth, I Lagzi, D Mathys, L Marot, A Braun, CE Housecroft, E C Constable: *Understanding the formation of aligned, linear arrays of Ag nanoparticles*, RSC Advances 6 (34), 28388-28392, 2016
- (iii) R. M. Walliser, F. Boudoire, E. Orosz, R. Tóth, A. Braun, E. C. Constable, Z. Rácz, I. Lagzi: *Growth of Nanoparticles and Microparticles by Controlled Reaction-Diffusion Processes*, Langmuir, 31, 1828-1834, 2015
- (iv) A Vágó, G Szakacs, G Sáfrán, R Horvath, B Pécz, I Lagzi: *One-step green synthesis of gold nanoparticles by mesophilic filamentous fungi*, Chem. Phys. Lett. 645, 1-4, 2016
- (v) D Zámbo, K Suzuno, S Pothorszky, D Bárdfalvy, G Holló, H Nakanishi, D Wang, D Ueyama, A Deak, I Lagzi: *Self-assembly of like-charged nanoparticles into Voronoi diagrams*, Phys. Chem. Chem. Phys. 18 (36), 25735-25740, 2016

4 Time programmed self-assembly of nanoscopic objects

Dynamic self-assembly is of great interest in the fields of chemistry, physics and materials science and provides a flexible bottom-up approach to build assemblies at multiscale levels. We propose a method to control the time domain of self-assembling systems in a closed system, from molecular to material level using a driving chemical system: methylene glycol sulfite pH clock reaction coupled to lactone hydrolysis (Figure 5). The time domain of the transient pH state (alkaline) and the time lag between the initialization of the reaction and the pH change can be efficiently fine-tuned by the initial concentration of the reagents and by the chemical composition of the lactone. The self-assembly of pH-responsive building blocks can be dynamically driven by this kinetic system, in which the time course of the pH change is coded in the system. This approach provides a flexible and autonomous way to control the self-assembly of pH responsive building blocks in closed chemical systems far from their thermodynamic equilibrium.

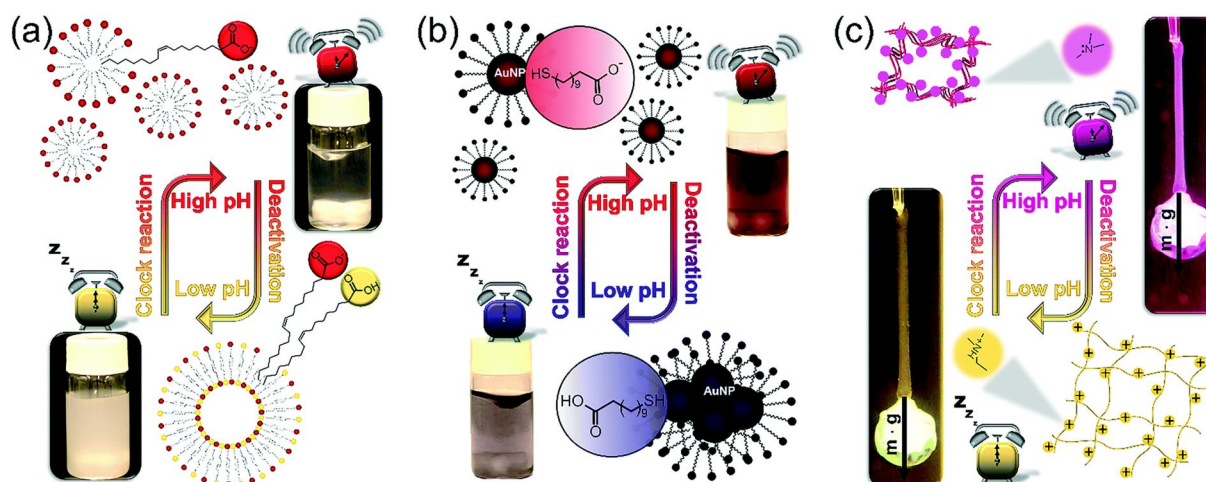


Figure 5 The concept of the time-programmed and precoded self-assembly of fatty acid molecules (oleic acid), gold nanoparticles, and polymer chains in a pH-responsive polyNIPAA-

based network. Lower and upper photographs show the states of the systems at the starting (low) pH and at the highest pH. (a) Reversible vesicle-micelle transformation of oleic acid molecules (low pH: vesicles - turbid solution, high pH: micelles - transparent solution), (b) reversible dissolution and aggregation of carboxyl terminated gold nanoparticles (low pH: aggregated NPs - blue solution with microscopic aggregates, high pH: free NPs - transparent red solution), (c) volume change (shrinking and swelling) of a hydrogel filament containing tertiary amine functional groups (low pH: swollen, highly elastic state; high pH: shrunken, more rigid state).

Related papers:

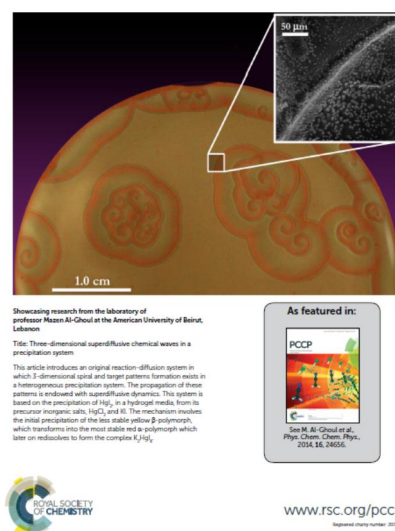
- (i) G Holló, B Dúzs, I Szalai, I Lagzi: *From Master-Slave to Peer-to-Peer Coupling in Chemical Reaction Networks*, J. Phys. Chem. A 121 (17), 3192-3198, 2017
- (ii) E Tóth-Szeles, J Horváth, G Hollo, R Szücs, H Nakanishi, I Lagzi: *Chemically coded time-programmed self-assembly*, Molecular Systems Design & Engineering, 2, 274-282, 2017

Results in nutshell

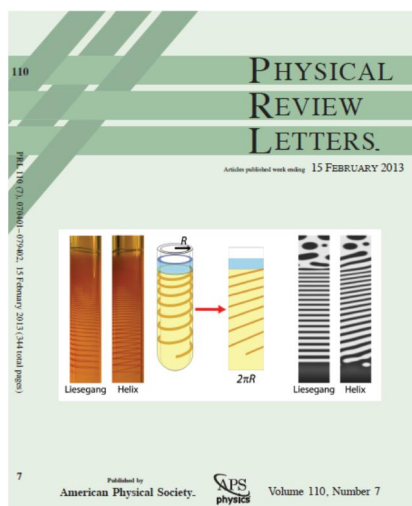
1. Published papers: **27 ISI (5.4 papers/year)**
2. Cover arts publication: **3**



K. Suzuno, D. Ueyama, M. Branicki, R. Tóth, A. Braun, I. Lagzi, Maze solving using fatty acid chemistry, *Langmuir*, 30, 9251–9255, 2014



M. Ayass, I. Lagzi, M. Al-Ghoul, Three-dimensional superdiffusive chemical waves in a precipitation system, *Phys. Chem. Chem. Phys.*, 16, 24656–24660, 2014



S. Thomas, I. Lagzi, F. Molnár, Z. Rácz, Probability of the emergence of helical precipitation patterns in the wake of reaction-diffusion fronts, *Phys. Rev. Lett.*, 078303, 2013

3. Editor's Choice paper: **1** (K. Suzuno, D. Ueyama, M. Branicki, R. Tóth, A. Braun, I. Lagzi, Maze solving using fatty acid chemistry, *Langmuir*, 30, 925169255, 2014)

4. Media coverage:

Science Daily (<https://www.sciencedaily.com/releases/2014/10/141027100346.htm>)

Chemistry Word (<https://www.chemistryworld.com/news/clock-watching-self-assembly-system-knows-when-to-start/3007633.article>)

4. Conferences and meetings: ~ 20