Introduction: Engineering of self-organized nanostructures

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The notion that the laws of nature might lead to the spontaneous generation of ordered structure can be found at least as early as Descartes' seventeenth century *Discourse on Method*.[1] The modern usage of the term self-organization dates back to 1947,[2] while the term nanotechnology appeared late in 1988[3] as a means of emphasizing the importance of nanometer-level precision in the top-down processing of submicrometer structures for electronics and optoelectronics. If one searches the Web of Science for "self-organization" and "nano-*," over 1000 entries appear, with the first of them[4] dating to 1991, the only article published on that juxtaposition of subjects that year.

Though typically observed, and perhaps most compelling, in biological systems, self-organization is ubiquitous over a broad spectrum of space and time. Traditionally, self-organized structures have been thought of as arising without human intervention. Recent work, however, has begun to reveal the factors that may induce and stabilize a desired self-organized structure, and we are now at the brink of being able to control the process of self-organization. In other words, self-organization is no longer confined to the realm of pure science but has begun to enter the domain of engineering as well. This tendency was accelerated when the self-assembly of tailor-made molecules was highlighted as one of bottom-up approaches to nanotechnology. The burgeoning of nanotechnology has become linked to recent progress in understanding how self-organized behavior can emerge from appropriately chosen initial and boundary conditions in nonequilibrium processes. From the viewpoint of modern thermodynamics, these trends in bottom-up technology can be regarded as a reprise of Schrödinger's view of the self-organization of life.[5]

This Focus Issue grows out of a workshop, "Self-Organization-Initiative Nano-Engineering (SINE)," organized by RIKEN and several other Japanese organizations, held at the RIKEN Wako campus outside Tokyo January 17–18, 2005. The workshop brought together scientists and engineers, both academic and industrial, from Japan and the West, to analyze the mechanism of self-organization in biological systems; to discuss a variety of approaches to controlled self-assembly based on the local interaction between smartly-designed molecules and materials; and to explore the self-organization of hierarchy by combining self-assembly and long-range interaction in nonequilibrium processes. This issue contains some of the most important papers from that workshop, spanning disciplines as "academic" as mathematics[6] and thermodynamics[7] to fields as applied as the design and manufacture of high density storage media.[8] The papers cover biology,[9,10] chemical dynamics,[11] crystal,[12] colloidal,[13] and polymer science.[14,15]

Readers are recommended to read the article of Arisaka[9] first to share with us a typical image of self-organization in nanotechnology. This report covers much of the latest knowledge about bacteriophage T4, an amazing molecular machine. T4 carries its genomic DNA and injects it into bacteria *without* using any fuel or external energy sources. Once injected, the DNA starts to produce the molecular components of T4 phage by the host system's machinery, leading to reproduction of its descendants. The sequence of the self-assembly processes is highly programmed. Most steps in the assembly are irreversible, but some are reversible. Knowledge about irreversibility is important for designing molecular LEGOs for constructing supramolecules[16] via noncovalent bonding.

The other contributions are classified into two categories: (dynamic) self-assembly and pattern dynamics, which is closely related to dissipative structure formation. As the term "self-organization" is often used for both self-assembly *and* dissipative structure formation, it is important to clarify the usage of these terms in this issue. Epstein and Vanag[11] compare self-assembly and dissipative structure by citing Ref. 17: "Self-assembled structures occur near or at equilibrium, have spatial periodicity with a wavelength of the same order of magnitude as the system components, involve physical forces of the order of a few kilojoules, and occur at a minimum of some thermodynamic function of state such as the

free energy. They often arise by a process of phase separation and can survive indefinitely without external energy fluxes. Dissipative or dynamical structures associated with chemical concentrations, in contrast, arise only far from equilibrium, can be temporally as well as spatially periodic, have wavelengths two to five orders of magnitude larger than the size of the system components, involve chemical forces (bonds) often tens of kilojoules in magnitude, depend upon reaction rates and the rate of energy dissipation, and require an external flux of energy to compensate for this dissipation. They originate via a dynamic instability, in which a state, often the homogeneous steady state, is unstable to infinitesimal perturbations and transforms to a differently structured state." Therefore, when the term "self-organization" is used rather than "self-assembly," it generally refers to the more complex process of dissipative structure formation.

The major fabrication techniques for bottom-up nanotechnology are summarized at the beginning of the article by Ishikawa:[13] self-assembly, self-organization, and manipulation by scanning probe microscopy (SPM) (Fig. 1 in Ref. 13). Then, analogous to the theory of crystal growth, he specifies the three concepts for precise fabrication of nanomaterials: (1) precise control of interparticle distances (formation of the crystalline structure), (2) specification of target assemblies (controlled formation of the critical cluster), and (3) location of target assemblies on the designated substances (heteroepitaxial growth on the substrate). The issue of precise fabrication of nanomaterials is converted into that of the nonlinear control of the nucleation process. A charged colloidal system governed by the Yukawa potential is studied as a model system, and the concept of dynamic templating of the critical cluster formation is proposed.

Pileni[12] reports on two collective properties of 3D supracrystals of inorganic nanocrystals. The size distribution of nanocrystals (Co or Ag) must not exceed about 13% for formation of fcc supracrystals. One case examined is the self-assembly of supracrystals of Co nanocrystals into well-defined column-shaped structures with a narrow size distribution under a magnetic field (0.25 T) applied perpendicular to the substrate. The formation of this columnar structure depends on the substrate-particle interaction. It is realized when highly-oriented pyrolytic graphite is used as the substrate. The other example is the coherent vibration among Ag nanocrystals in a supracrystal, which is shown by the sharp line profiles of Raman scattering spectra.

For Yabu *et al.*,[15] self-organization is a dynamic process of spontaneous formation of an ordered structure far from thermodynamic equilibrium. They develop a new physical procedure for preparation of polymeric nanospheres. Nanoparticles of polystyrene-isoprene block-copolymer are prepared from a tetrahydrofuran (THF)-water solution by slow evaporation of a "good" solvent, THF. Similar to the microphase separation in a bulk film, well-developed lamellar nanostructures are observed. Evaporation of the good solvent induces a slow drift in the solubility parameter. This observation implies that their procedure is equivalent to the thermal or solvent annealing processes that are very efficient for developing highly-ordered phase separated structures. The wide applicability of this procedure is demonstrated by preparation of nanoparticles of RNA-cationic amphiphile complexes.

Electric fields are often applied to induce instability in polymeric systems above the glass transition temperature, resulting in pillar formation. The wave number is predicted by linear stability analysis and 3D simulations. Leach *et al.*[14] studied a trilayer system composed of polystyrene (PS)/poly(methylmethacrylate) (PMMA)/air sandwiched between two different electrodes, aiming to provide insights into the complex concerted effects of dewetting and electrostatic pressure. When a low dielectric material is placed next to a high dielectric material, the interface is pushed towards the lower dielectric material under the electric field and, consequently, PS pillars (some microns in diameter) coated with PMMA are obtained. When the viscosity of PS is sufficiently high, large circular rings of PMMA are observed with some ordered PS structures within them. In this way by using electric fields, micro- and nanostructured hierarchical materials can be produced. Self-organization of a hierarchical structure is one of the important topics of this Focus Issue.

Self-assembly and self-organization are smart procedures for obtaining a patterned medium at a low cost. However, controlling the position is difficult. This disadvantage can be overcome by combining a top-down procedure. Naito[8] describes a method of artificially assisted self-assembly (AASA) aimed at industrial production of ultrahigh density data storage (it is predicted that the density of data storage will reach 1 Tb/in.^{2} around 2010-2013). By nanoimprinting, a top-down method, spiral patterns with a 400-nm-width groove and a 110-nm-depth are transferred to a resist film on a CoCrPt film (a Ni master disk for nanoimprinting was prepared by photoprocessing). A solution of PS-PMMA diblock copolymer is cast into the groove, then annealed to prepare self-assembling PMMA dots that are selectively removed by an oxygen plasma treatment in preparation for further treatment (the block-copolymer lithography), as the use of AASA and similar methods is seen in technologies for MEMS and nanodevices as well.[18]

The morphology of microphase separation of PS-PMMA block copolymer is very similar to the reaction-induced stationary structures known as Turing structures, though Turing structures belong to the class of dissipative structures, which are supported at the expense of energy dissipation. There has been much discussion of the similarity between the self-assembled structure of block copolymers and that of Turing patterns. Modern thermodynamics tells us that, within the linear regime, i.e., so far as the Onsager reciprocal relations hold, there exists a thermodynamic potential: the entropy production. As the Turing structure is a time-independent structure, the entropy production may constitute the thermodynamic potential, analogous to the Gibbs free energy near equilibrium. If so, then we can get a powerful guide for pattern processing in nanotechnology. Mahara *et al.*[7] report the entropy production in a self-replicating process of spots leading to a Turing structure. This replication process can also be regarded as a dissipative-structure assisted self-assembly, which increases the complexity and a hierarchical structure in the system. The reversible version of the Gray-Scott model is shown to be a good tool for thermodynamic

consideration of pattern formation and pattern dynamics in reaction-diffusion systems. The authors suggest that how far the open system is driven from equilibrium is determined by both the environmental constraints and the plasticity of the system itself.

Nishiura *et al.*[6] study mathematically an extended version of the Gray-Scott model, in which an inhibitor w is added to the original two-component system. Taking into account the fact that splitting dynamics is one of the driving forces in creating many particlelike patterns from a single seed, they focus on the collision dynamics of traveling spots in a three-component system. They illustrate a typical example of the change of transition caused by destabilization of the scattor, where a scattor is a hidden saddle that provides "traffic control" of orbits during the collision process. The concept of scattor is universal. Three scattors are found in the three-component Gray-Scott system: a peanut, a large- and a small-disk.

The Belousov-Zhabotinsky (BZ) reaction is the most thoroughly studied oscillating chemical reaction. It serves as a prototype system for a wide range of phenomena in nonlinear chemical dynamics. Epstein and Vanag[11] introduce a new kind of BZ reaction, using water-in-oil microemulsions as reacting media. The ratio $\omega=[H_2O]/[AOT]$ determines the average radius of the water droplet cores, which is roughly equal to $R_w=0.17\ \omega(\mathrm{nm})$. This medium called the BZ-AOT system, shows a rich variety of spatio-temporal patterns: Turing patterns, spirals and antispirals, accelerating waves, segmented (spontaneously broken) waves, packet waves, and localized structures. A model for the BZ-AOT system is proposed. The BZ-AOT system thus provides a laboratory model and hints for understanding the spatio-temporal dynamics of coupled nanoreactor systems.

One of the major fields of application of nanotechnology in the future may be information processing and learning, similar to the processes in our brain realized by neuronal excitable media. Sooner or later, if the system becomes highly integrated, then there will appear a new difficulty that is different from those of data storage: the fidelity of signal transmission. The final contribution by Larter and Craig[10] highlights this issue. The synapse should rightly be thought of as "tri-partite," i.e., comprised of a presynaptic neuron, a postsynaptic neuron, and an astrocyte, which mediates communication between these two. Astrocytes can convert neurotransmitter signals from neurons into bursts of calcium. Astrocytes are therefore chemical "FM transmitters." The authors study the calcium bursting mechanism in astrocytes and propose a new model they name Glutamate-Induced Glutamate Release (GIGR). The model involves two positive feedback processes, in which the key feedback species are the calcium ion and glutamate.

We hope that this Focus Issue will pique the interest of the readers of CHAOS and will generate new discussions between the disciplines of nonlinear dynamics and materials science. Such collaborative activity is needed to generate further progress in bottom-up nanotechnology, and to enhance our understanding of self-organization in general.

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