



Dynamic nanoarchitectonics: Supramolecular polymorphism and differentiation, shape-shifter and hand-operating nanotechnology



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ABSTRACT

Recently proposed novel nanoarchitectonics concept is based on the unification of nanotechnology and other constructive sciences such as supramolecular chemistry including self-assembly/self-organization to provide the functional nanostructures and materials through architecting efforts of nano-sized components. In this short review, we focus on the structural changes and related dynamic functions with the terminology of dynamic nanoarchitectonics. We will cover selected topics on supramolecular polymorphism, supramolecular differentiation and dynamic-motion-based functions. Such phenomena have been observed in shape-diverse assemblies of amphiphilic tripeptides, polymorphisms in assemblies and crystals of fullerene derivatives such as supramolecular differentiation for the spontaneous growth of tails (tubes) from the egg of fullerene assemblies. Similarly, they have also been realized in self-propelled nano- and micromotors and robots, self-powered cargo delivery system with several bio and supramolecular components, manipulation of liquid slugs within photoactive tubular microactuators, materials with ameba-like motions through autonomous periodic sol-gel transition, molecular machine regulation by hand-motion-like macroscopic actions (hand-operating nanotechnology) and mechanical tuning for molecular receptors functions. These examples inspire us to create new functional materials with truly life-like activities through nanoarchitecting simple nano/molecular units.

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1. Introduction

Recently, a novel concept, nanoarchitectonics has been proposed [1,2]. The nanoarchitectonics concept is based on the unification of nanotechnology and the other constructive sciences such as supramolecular chemistry including self-assembly/self-organization to provide functional nanostructures and materials through architecting efforts of nano-sized components (Fig. 1) [3,4]. The nanoarchitectonics process includes high-resolution controls of the arrangements of atom/molecule, chemical-reaction-based conversions of molecules/materials, physical/chemical processes for the self-assembly/self-organization and bio-related manipulation and organization. Because these processes completely overlap with the current existing materials sciences [5,6–9], organic chemistry [10,11], nanotechnology [12–15] and biological sciences [16–18], the nanoarchitectonics concept has been applied to many disciplines of science and technology including functional materials sciences [19,20], analytical chemistry and sensors [21,22],

device and nanomachine technologies [23], energy/environmental sciences [24,25] and bio-oriented applications [26,27].

Unlike architecture productions and craftworks in macroscopic worlds, architectonic processes with nano-size components cannot avoid the uncontrollable disturbances and fluctuations from surroundings and even from interacting molecules including thermal fluctuation, statistical uncertainty and unpredictable effects. Therefore, harmonization becomes crucial for the various interactions and effects to bring target components/materials into desirable structures and functions in the nanoarchitectonics process [28]. Generally speaking, this situation is similar to those found in biological systems in which biomolecules are synthesized on the basis of programmed sequences of DNA and are organized through combination of supramolecular interactions. The produced biomolecules and their assemblies are actually working under the influences of thermal fluctuations through well-harmonized actions. The nanoarchitectonics concept and biological strategies share these two features, architecting processes from nano/molecular units and functions based on the harmonized interactions. Nanoarchitectonics could be regarded as a navigator from materials to life [29,30]. The above-mentioned discussion suggests that the nanoarchitectonics approach is not only a methodology to make functional materials but can also become a strategy to construct material systems with life-like features.

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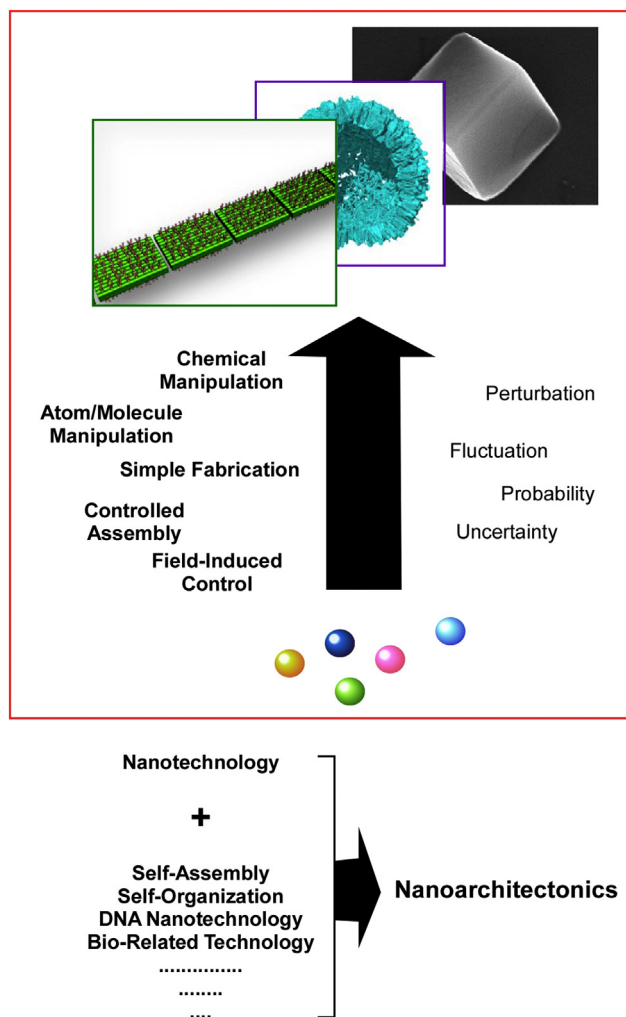


Fig. 1. Outline of the nanoarchitectonics concept.

In this short review, we focus on the structure changes and related dynamic functions with the terminology of dynamic nanoarchitectonics and explain the selected topics on supramolecular polymorphism, supramolecular differentiation and dynamic-motion-based functions. For supramolecular polymorphism, several systems to create self-assembled objects with totally different shapes from one identical molecule are exemplified. Examples for egg-to-tadpole-like shape changes during the self-assembling processes are introduced in the section of supramolecular differentiation. Several types of dynamic functions including molecular-level motions and visible-level materials motions will be discussed. In the final section, attempts in reverse direction, *i.e.*, dynamic control of nano/molecular functions by macroscopic mechanical motions including dynamic tuning of molecular structures will be discussed, which would become an important key to explore the advanced functions. These examples may guide us to create new functional materials with truly life-like activities through nanoarchitecting simple nano/molecular units.

2. Supramolecular polymorphism: from a single unit to diverse assemblies

Perfectly regulated self-organization processes would give one organized assembly with well-defined shape from one particular unit. In contrast, assembling process allowing certain ambiguity as seen in the nanoarchitectonics concept may result in the assembled structures with various shapes. It can be regarded as supramolecular polymorphism.

In most of the cases of peptide assemblies and protein folding, the produced objects finally reach to an energy minimum state to give one structure with defined shape. Inclusion of misfolded peptides and protein segments may give wrong (different) shapes. Possibilities of such structure diversity increase when peptide sequences become shortened. Examples of diverse-shape assemblies of amphiphilic tripeptides based on this concept are displayed in Fig. 2, which was accomplished through a simple process of casting with different solvents [31]. The amphiphile has a tripeptide segment of AlaAlaGlu with hydrophilic quaternary ammonium group and hydrophobic long alkyl chains (C_{12}) at N and C terminal, respectively. Casting of its aqueous, $CHCl_3$ and CCl_4 solutions resulted in objects with completely different shapes, thin needles, flat patterns, and thick rods as supramolecular polymorphism, respectively, although the used molecules and casting conditions were identical.

This molecular unit has two major assembly motifs, β -sheet-like hydrogen bonding networks at the tripeptide segment, and alkyl chain solidification. Formation of these assembling structures depends significantly on the polarity of medium. Upon transfer from solution state to dried state, differences of occurrence timing of these interactions drastically alter their assembling structures. In polar medium water, this amphiphilic peptide molecule forms tight assembly with parallel β -motif of the tripeptide moiety and bilayer structure with well-packed alkyl chain to form thin-needle or fiber assemblies. Even after evaporation of the solvent upon casting on a solid surface, thin-needle-type assemblies are maintained. In contrast, only the hydrogen bond motif is formed but the bilayer structure is weakly formed with fully solvated alkyl chains in highly non-polar medium, CCl_4 . Solidification of alkyl chains are promoted upon CCl_4 solvent evaporation, resulting in the growth of thin needles into thick rod structures. In polar medium $CHCl_3$, the amphiphilic peptide molecules are well dispersed in its diluted solution, and both the interactions are strengthened only upon the solvent evaporation, resulting in the flat film structure.

Similar supramolecular polymorphism can be observed with various designs (types) of unit molecules. Nakanishi and coworker used alkylated fullerene molecule as an assembling unit [32]. This molecule has sp^2 -carbon-rich parts (fullerene moiety) and sp^3 -carbon-rich part (alkyl chains). In addition to the conventional hydrophilic/hydrophobic discrimination these moieties have different affinities to aliphatic and aromatic solvents. Therefore, assembly of this alkylated fullerene molecule leads to the huge varieties of morphologies of the resulting assemblies. In fact, microscopic vesicles, fibers, discs and cones can be fabricated through a solution-casting of the same molecular unit by simply modifying solvents.

A liquid-liquid interfacial precipitation (LLIP) method has been used as a simple but superior and versatile method to fabricate various molecular assemblies using different affinities of the unit molecule towards the two solvents. Various-shaped crystals can be obtained from ideal zero-dimensional objects, fullerenes (C_{60} or C_{70}), by the LLIP, which is driven by the supersaturation related to very low solubility of fullerene at the interface of good solvent and poor solvent of fullerene [33]. For example, Miyazawa and coworkers have demonstrated production of one-dimensional fullerene crystals in rod or tube shapes using this method [34]. Such one-dimensional fullerene crystals can be highly aligned with Langmuir-Blodgett [35] and vortex Langmuir-Blodgett method [36] and employed as cell culture media with controlled alignments and differentiation.

Fullerene crystals with different dimensions can be easily fabricated by simply changing solvent systems. For example, two-dimensional objects with well-defined hexagonal plate-like morphology containing bimodal pore structure is displayed (Fig. 3) [37]. In this case, fullerene solution was prepared in a mixture of two different good solvents (benzene and carbon tetrachloride) and fullerene crystal were grown by LLIP method using isopropyl alcohol as a poor solvent. Under the optimized condition, two-dimensional hexagonal sheet morphology comprising of macropores (few hundred nanometers) on the surface

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