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Katsuhiko Ariga¹,²,a) and Lok Kumar Shrestha¹

AFFILIATIONS
¹World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan
²Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan

a)Author to whom correspondence should be addressed: ARIGA.Katsuhiko@nims.go.jp

ABSTRACT

Nanoarchitectonics has been paid much attention as an emerging concept to architect functional materials from molecular and nanounits through the combination of nanotechnology-oriented strategies and supramolecular-chemistry-like methodologies. This perspective article aims to figure out important keys for materials nanoarchitectonics. In the initial part, recent trends in materials nanoarchitectonics upon supramolecular self-assembly are overviewed. The overview processes extract several key words including dynamic natures, dimensional controls, and interfacial processes according to the following sections: (i) preparation of assembled structures and conversion into nanostructured materials, (ii) dynamic structural transformation to hierarchic materials, and (iii) material preparation and functions with dynamic flows at interfacial media. Not limited to the material production, dynamic processes at the interface can be also connected with forefront functions such as tuning of molecular receptors and mechanical controls. This perspective article can conclude that fabrication of functional materials and controls of nanosystems would be well-considered on the basis of these three key terms.

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I. INTRODUCTION

Although there are several demands in current societies, considerable parts of them can be solved with innovations and advancements of materials. Necessary matters with social demands are dispersed in a wide range of research efforts including material synthesis and production,¹ fine structure fabrications,² ecological uses of material sources,³ environmental protection and remediation,⁴ energy production and storage,⁵ and biological/biomedical treatments.⁶ High efficiency, less energy consumption, less emission, low-cost, process integrity, sufficient stability, user friendly, and biocompatibility are often requested as satisfied factors.⁷ These requirements cannot be always accomplished with simple synthetic procedures alone although continuous success has been made in organic synthesis⁸ and inorganic material preparation⁹ as basic science.

The same materials with different structures often exhibit totally different properties. Performances of the functional materials of the same components have unavoidable dependences of structural integrations of the components. Exploration of material functions in advanced levels cannot be achieved only with innovations of the materials themselves. Fabrications of material structures with structural precisions at atomic, molecular, and nanolevels becomes crucial to make materials optimized for the targeted functions. However, conventional microfabrication and nanofabrication would not be always capable of controlling molecular-level structural integrations that can be accomplished by other scientific disciplines such as supramolecular chemistry on the basis of self-assembly and self-organization.¹⁰ A novel concept to architect functional materials from molecular units and nanounits by combining nanotechnology-oriented strategies and supramolecular-chemistry-like methodologies is required. This essential concept corresponds to an emerging concept, nanoarchitectonics.¹¹

The nanoarchitectonics concept in this meaning was initiated by Aono.¹² Successful developments of nanotechnology provide us to observe structures with incredibly high precisions
and to manipulate small objects including a single atom. These advanced skills are now coupled with widely applicable scientific knowledge in supramolecular chemistry, organic synthesis, chemical physics, and even biotechnology to create methodology for material constructions from nanounits, which is called nanoarchitectonics (Fig. 1). The nanoarchitectonics methodology provides ways to fabricate functional materials through combining atom/molecular manipulation, chemical synthesis, microfabrication/nanofabrication, self-assembly/self-organization, field-controlled arrangements, and biorelated processes. 

Because the nanoarchitectonics concept uses the process common for a wide range of research fields, this concept has been applied to various targets in functional material productions such as materials synthesis,45–47 functional structure fabrications,48–50 sensing,51,52 catalysts,53,54 energy-related applications,55–58 devices,59–61 drug delivery,62,63 biofabrications,64,65 cell regulations,66,67 and the other biological/biomedical applications.68–71

One distinct difference in the nanoarchitectonics strategy from the microfabrication/nanofabrication would be allowance of high flexibility. Various fluctuations and uncertainties such as thermal fluctuation, statistic uncertainly, quantum effects, and highly integrated mutual interactions are common in nanoscale worlds. In the nanoarchitectonics concept, target materials are architected through harmonization of several effects and processes upon unavoidable inclusion of these unpredictable effects.72,73 Therefore, the nanoarchitectonics processes would be suitable for functional materials with dynamic natures. In addition, process harmonization is often useful to construct hierarchic functional structures.

Although the nanoarchitectonics approaches are not fully established yet, it would be meaningful to overview recent progress according to several methodology lines. This perspective article is focused on materials nanoarchitectonics especially upon supramolecular self-assembly. Section II overviews the recent trends of self-assembly research to extract what have to be solved with the nanoarchitectonics concept. Following this initial section, three methodologies from molecules to materials are explained: (i) preparation of assembled structures and conversion into nanostructured materials; (ii) dynamic structural transformation to hierarchic materials; (iii) material preparation and functions with dynamic flows at interfacial media. These examples would reveal important key terms, dynamic, hierarchic, and interface in supramolecular nanoarchitectonics for functional materials.

II. RECENT TREND OF SELF-ASSEMBLY RESEARCH

A. Recent examples of self-assembly research with material varieties

Although syntheses of covalently connected polymers with various functional groups sometimes become tough processes, assembling rather synthetically simple units into pseudoconjugated materials would be an easier approach to produce functional systems. Forming extended π-electron systems through self-assembly of simple and small galator molecules is one of the attractive research targets. Recently, Ajayaghosh and co-workers have overviewed the extended π-electron systems through self-assembly of borondipyrromethene (Bodipy) dye derivatives (Fig. 2).74 In addition to the synthetic easiness of the Bodipy derivatives, these chromophores possess advantageous photophysical natures including photostability, good molar absorptivity, and high quantum yields in fluorescence. Their structural features with rigid aromatic backbone

FIG. 1. Outline of nanoarchitectonics methodology for ways to fabricate functional materials from nanounit components through possibly combining atom/molecular manipulation, chemical synthesis, microfabrication/nanofabrication, self-assembly/self-organization, and so on.

FIG. 2. Formation of extended π-electron gel systems through self-assembly of borondipyrromethene (Bodipy) dye derivatives.
lead to facile assemblies with a certain kind of structural modification. The latter nature of the Bodipy assemblies resulted in possible tuning of their electronic performances in a wide range from the UV-vis region to the NIR region. Owing to these characteristics, the self-assembled π-electron materials with the Bodipy derivatives have potential usages in bioimaging and bio labeling as well as well-expected photovoltaic applications.

Importance of molecular designs can be recognized in a wide range of self-assembled materials. As Takimiya and Nakano reviewed for thiophene-fused naphthalene diimide derivatives as n-type organic semiconductors, molecular designs are crucial to form molecular stacking favorable for intermolecular π-π overlap in their assembled solids. The rigid planar molecular design over the whole π framework is advantageous for π-π overlap between neighbor molecules for better conductivity. These compounds can be good building blocks for organic electronics with supramolecular nanoarchitectures. Sada developed gel assemblies with supramolecular regulation of swelling and collapsing. In one of their approaches, size, shape, and crosslinking points of polymer gels can be controlled through association with metal-organic frameworks (MOFs). The resulting anisotropic volume expansion is beneficial to realize size and directional controls of gel expansion.

Ichikawa and co-workers synthesized dicationic amino-acid-type ionic liquids as media for self-assemblies and investigated assembling behaviors of amphiphilic molecules in these ionic liquids. In this circumstance, lyotropic liquid crystalline regions of the amphiphile assemblies are effectively expanded through cation bridging. The obtained results indicate the importance of the design of assembling media for desired self-assembled nanoarchitectonics. Medium control is also important for self-assembling processes in addition to the molecular designs of components themselves.

Materialization of controlled self-assembly results in various functions. One of the outputs is molecular imprinting as recently reviewed by Komiyama et al. Molecular assembly, fixation of materials structures, and removal of molecular templates lead to the formation of well-controlled molecular cavities for specific molecular recognition. The imprinted materials can be controlled by external stimuli such as photo, thermal, and pH. The molecular imprint nanoarchitectonics can be applied for more sophisticated targets such as protein and DNA for biosensing and controlled drug delivery.

Supramolecular nanoarchitectonics based on self-assembling processes is not limited to the self-assembly of organic molecules. As examples of precise crystalline assembly, Pileni have discussed sensitive mechanisms for supramolecular growth using 5 nm Au nanocrystals as building blocks in the self-assembling process. Only faint factor of trace amount of water significantly alters the average internanocrystal distance. The other influences such as solvent evaporation, its vapor pressure, and coagent reagent amounts are related with transition from film structures to unified-shaped supracrystals. Triangular supracrystals are formed upon homogeneous growth of a single domain. In contrast, polycrystalline nanocrystals result in the formation of film structures upon heterogeneous growth process. Hierarchic supracrystal growth can be induced through changes from homogeneous to heterogeneous processes.

Among self-assemblies of biomolecules, short peptides can be regarded as versatile building molecules to provide a wide variety of nanostructures with various functions only with simple molecular designs of the components. Yan and co-workers have summarized recent results on peptide-based nanoarchitectonics in their recent review article, in which three major functions, biomimetic photosystems, optical waveguiding, and phototherapy, are highlighted. In addition, coassembly of peptides with a photokilling dye and manganese(II) ions creates nanoarchitectonics with capabilities of magnetic resonance imaging and tumor photodynamic therapy. Mihara and co-workers reviewed medical usages of calcium ion-responsive peptide assemblies such as nanofibrous structures and hydrogel materials for applications including cell cultures and drug delivery. Because these peptide assemblies provide environments similar to extracellular matrices, applications for tissue engineering is well expected.

Use of filamentous viruses (M13 phages) as building blocks for self-assembly was demonstrated in a recent review article by Sawada and Serizawa. Genetic engineering of M13 phages enables to display peptides and proteins on their surfaces. Formation of liquid crystalline materials result in the utilization of display capability for a wide range of applications including biomedicines, sensors, and devices. As summarized in a recent review article by Kobayashi and Okano, assemblies of living cells on temperature-sensitive polymer, poly(N-isopropylacrylamide), creates transplantable two-dimensional cellular tissues.

Three-dimensional cell-architectonics is also possible, and further integration with the other technologies would lead to formation of three-dimensional functional organs.

B. Key features of self-assembly research

As seen in the above-mentioned examples, self-assembly processes are widely applicable to architect functional materials and systems. However, some unsolved problems and unexplored features remain as described below. Reviewing these examples reveals several key terms toward the future direction of supramolecular materials with self-assembly processes. Representative keywords for future self-assembly research would be (i) dynamic behavior, (ii) dimensional control, and (iii) interfacial process. These keys often include uncertainty of temporal and spatial dynamicity and fluctuations. Therefore, future directions for material developments upon self-assembly have to be supported by the supramolecular nanoarchitectonics.

Hiraoka exemplified some unsolved problems in self-assembly in his recent review article in the cases of application of quantitative analysis on the self-assembly process for understanding of coordination self-assembly and formation of discrete molecular self-assemblies through weak, nondirectional molecular interactions, van der Waals interaction, and the hydrophobic effect. Because the assembling processes dynamically take several possible pathways including kinetic trap, self-assembling processes become much more complicated than expectations. Self-assembly processes are regarded as events on an energy landscape rather than those with a simple reaction coordinate. Designing complimentary molecular surfaces are effective to achieve discrete assemblies in water.

Dhiman and George gave their views on temporally controlled supramolecular polymerization in their recent review article. As they emphasized, precise controls of the self-assembled polymeric structures without covalent bonding, supramolecular
polymers, have been paid much attention with regulations of length and its dispersity analogous to the living polymers of covalent species. Living supramolecular polymerization is generally maintained through temporally and dynamically switching of structures and natures of their monomers and polymers. Kinetically dominant states of molecules for off-pathway or on-pathway intermediates create kinetic and metastable traps in nonequilibrium and nondissipative fashions. These dynamically controlled self-assembling processes are not fully explored yet, but further advancements to supramolecular materials with spatio-controls and temporal regulations are anticipated.

Instructed-assembly is defined as a self-assembly process for ordered supramolecular structures with at least one trigger event. He and Xu introduced use of instructed-assembly for the control of cell fate in their recent review article (Fig. 3). In biomimetic processes, dynamic transformation from one equilibrium to another is often crucial that can be driven by instructed-assembly with spatiotemporal control of biological events. Usages of processes based on instructed-assembly in various biomedical applications such as tissue engineering, molecular imaging, and cancer therapy are expected. Instructed-assembly can dynamically link multiple self-assembling events simultaneously, resulting in biomimetic active processes. Because dynamic formation and breaking of noncovalent and covalent bonding become possible in instructed-assembly, this concept can be widely used in various scientific disciplines including chemistry, materials science, and biomedical fields.

Another important factor to develop functional self-assembled materials is the dimensional control. Haketa and Maeda recently summarized their approach on dimension-controlled π-electronic ion-pairing self-assemblies. Anisotropic dimensionally controlled ion-pairing assembly is driven by electrostatic interactions together with weak noncovalent interactions. Use of π-electronic ion species resulted in the formation of mesophases with tunable electronic properties in their crystals and soft materials. Upon appropriate molecular designs, π-electronic ion pair provides dimension-controlled self-assemblies in various modes. Alternate stacking of positive and negative species leads to assembling mode of charge-by-charge assemblies. This charge-by-charge assembling mode is advantageous to form columnar self-assemblies based on electrostatic attraction to maintain π-π stacking. In contrast, identical charge species can stack to form charge-segregated assemblies upon overcoming the electrostatic repulsions. In many cases, these charge-by-charge mode and charge-segregated mode are cocontributed to assembling structures. Controlling these assembling modes would result in dimensionally controlled assemblies possibly with advanced optical and electric properties.

Shimizu and co-workers have been working on preparation of one-dimensional discrete nanotubes on the basis of self-assembly of organic molecules. According to his recent review article, chemical structures of the building blocks affects the formation mechanisms of nanotube objects including tolling of membranes or sheet, formation mediated by nanoring or nanotoroid structures, and...
Asanuma and co-workers proposed the use of DNA duplexes assembly as ideal one-dimensional scaffold to deeply analyze the photochemical events.\(^{90}\) DNA duplex can be regarded as a one-dimensional soft crystal with crystal-like rigidity and additional advantageous features of sufficient water solubility and sequence programmability. Desirable chromophores can be immobilized into DNA duplex assemblies by introducing the D-threoninol residue where number, distance, and orientation of the chromophores can be regulated. For example, arrangements for fluorescent resonance energy transfer with donor pyrene and acceptor perylene were nanoarchitected and subjected to photochemical investigations for verification of the corresponding theories. They also proposed nanoarchitectonics of energy harvesting mimics using circular DNA duplexes.

Dimensionally controlled entanglements of coordination polymers of actinides with organic ligands were discussed by Shi and co-workers.\(^{91}\) Entangled structures are nanoarchitected with various supramolecular motifs such as polyelectrolynes, parallel interpenetration, polycatenation, and Borromean ring. Pseudorotaxane ligands are used for synthesis of actinide polyelectrolynes, and frameworks with inclined polycatenation require templates and/or regulated backbones in their syntheses. The synthesized materials can be possibly subjected to many kinds of applications including radiation detection, radionuclide separation, and photocatalysis. Flexible natures of these dimensionally controlled entangled supramolecular structures are also appropriate for stimuli-responsive smart materials.

Fabrication of well-defined two-dimensional structures is important from several viewpoints such as coupling with device and sensor structures.\(^{12,293}\) In addition, interfacial science plays crucial roles in two-dimensional supramolecular nanoarchitectonics. Notably, surface energetic effects are essential in the determination of the domain structures in two-dimensional systems. Recently, Oishi and co-workers demonstrated the regulation of two-dimensional domain sizes from nanoscale and micrometer-sizes formed through self-assembly and phase separation within the mixed monolayers of carboxylic acid with perfluoroalkyl chains and guanidinium amphiphile with hydrocarbon chains (Fig. 4).\(^{28}\) Surface free energy can be altered depending on pH and ionic strength of subphase, and domain size and shapes were regulated by the balance between line tension and dipole density. Krafft reviewed self-assembled behaviors of fluorocarbon-hydrocarbon diblock compounds at two-dimensional plane of the air-water interface.\(^{97}\) These diblock compounds spontaneously form circular mesoscopic domains even at zero surface pressures. The monolayer assemblies at the air-water interface are rheologically elastic at all the surface pressures. Two-dimensional physical gels were formed even at zero pressures.

Fabrication of self-assembled monolayer (SAM) is a technically useful method to control the surface properties of materials. The SAM method sometimes allows us to immobilize short-chain compounds to the surface although the Langmuir-Blodgett (LB) method at the air-water interface essentially requires compounds with longer chains. Hasegawa and co-workers successfully immobilize short (C₆) fluorocarbon chains to water-and-oil repellency by the SAM method.\(^{98}\) Their strategy is based on the stratified dipole-arrays theory that indicates surprisingly low surface energy can be obtained even for the short fluorocarbon compound. Suda summarized strategies for photocontrollable molecular devices through immobilization of photoresponsive SAM structures on the device surface.\(^{97}\) The nanoarchitectonics design of molecular dipoles and their arrangements in the SAM structure is the crucial factor to manipulate interfacial electronic structures. Control of the dipole status upon photostimuli can create photocontrollable devices such as photocurrent-responsive organic superconducting transistors.

Seki also reviewed photoresponsive properties of the monolayers of soft materials such as polymers including azobenzene and diarylithene units as photoresponsive chromophores and their use in motional controls.\(^{98}\) The azobenzene moieties and diarylithene units exhibit significant changes of their molecular structures through photoisomerization. Accumulation of these molecular structural changes in molecular assemblies confined within two-dimensional media causes macroscopic motional behaviors. In addition, more precise motional controls with spatial-temporal manners are also possible in submicrometer levels.
III. NANOARCHITECTONICS FROM SELF-ASSEMBLY TO FUNCTIONAL MATERIALS

The above-mentioned examples specify the distinct features of self-assembling processes in recent research efforts, including dynamic natures, dimensional controls, and important roles of the interfacial processes. These features are also reflected in conversion from self-assembled structures into nanostructured materials as seen in examples described in Secs. III A–III C.

A. Preparation of assembled structure and conversion into nanostructured materials

One of the widely recognized successful nanoarchitectonics methodologies for the conversion of self-assembled structures into nanoregulated materials is the template synthesis. In template synthesis using supramolecular assemblies, flexibly adjustable structural features of supramolecular assemblies can be transferred into functional materials with high structural precisions and integrations.

Yamauchi and co-workers demonstrated fabrication of mesoporous metal oxides in various compositions through template synthesis using stable polymeric micelles. Spherical micelles of triblock copolymer, poly(styrene-b-2-vinyl pyridine-b-ethylene oxide), basically have dynamic nature, but their hydrophobic poly styrene moieties are kinetically frozen to form stable cores of the micellar structures. In addition, poly(2-vinyl pyridine) blocks around the polystyrene core have strong interaction with inorganic precursors, which work as the media appropriate for inorganic reaction. High thermal stability nature of these micelles is also useful for high-temperature synthesis to provide highly crystalline mesoporous materials. Dynamically optimum micelle structures can provide mesoporous metal oxides materials with tunable wall thickness, pore sizes, and crystallinity, which are advantageous for the fabrication of mesoporous materials for various functions.

Mesoporous carbon materials can also be synthesized through direct carbonization of self-assembled coordination assembly, metal-organic frameworks (MOFs). Torad et al. prepared nanoporous carbon particles with a diameter of 50 nm from MOF structures. Because the prepared nanocarbon particles have high biocompatibility, they are suitable for biorelated applications such as drug delivery. Tuning of particle shape and size with surface functionalization would optimize the capability of endocytosis of the particles. Yamauchi and co-workers nanoarchitected integrated layer-by-layer materials, coordination polymers, and graphene oxide nanosheets by the one-pot self-production process. In the reported procedure, surfaces of graphene oxide nanosheets worked as effective nucleation site for Ni-based cyanide bridged coordination polymers to form regular layer-by-layer nanoarchitectures upon optimization of crystallization conditions. Further thermal treatments resulted in the formation of lamellar materials with excellent electrocatalytic activity for oxygen reduction reaction with outstanding durability. This one-pot self-production strategy would be adopted to the other functional two-dimensional materials.

Hierarchic porous structures can be directly synthesized through self-assembly of functional molecules such as fullerene at interfacial processes. Preparation of fullerene self-assembly materials with various dimensionalities has been reported using the liquid-liquid interfacial precipitation method. Shrestha et al. successfully fabricated C60 fullerene assembling materials in the regular two-dimensional hexagon shape with hierarchic nanopore nanoarchitectures (Fig. 5). Interfacial precipitation of C60 molecules at the liquid-liquid interface of isopropyl alcohol and a mixture of benzene and carbon tetrachloride under optimized conditions resulted in the formation of regular two-dimensional hexagon nanosheets of C60 assembly. Upon modification of the mixing ratios between benzene and carbon tetrachloride, porosity (i.e., electroactive surface area) can be flexibly tuned. The formed pore walls are basically crystalline with bimodal hierarchical nature with mainly consisting of macropores and mesopores. Hierarchic pore structures would provide opportunities for various advanced functions such as photovoltaic devices through inclusion of appropriate partner molecules such as porphyrins.

Just by changing combinations of liquid phases, fullerene assembly materials drastically altered their shapes. For example, C60 self-assembly at the interface between isopropyl alcohol and dodecyl benzene resulted in the formation of bitter-melon-shaped crystals including nanoporous structures. The fabricated high-surface-area materials were subjected to vapor sensing through casting the materials onto the electrode surface of quartz crystal microbalance (QCM). Frequency-based QCM sensing exhibited higher affinities to aromatic organic vapors in sensitivity order of aniline > toluene > benzene > ethanol > hexane > cyclohexane > methanol > water, which is probably based on favorable adsorption of aromatic gas molecules onto sp2-rich C60 surfaces.

Fabrication of nanoporous materials by self-assembling processes is not limited to conventional organic and inorganic substances. As one example for biomolecule-based nanoporous materials, Vinu and co-workers reported preparation of nanoporous protein films and their uses for sensing of acidic gases. In the first process, highly aligned self-assembled films of polystyrene microbeads were prepared on the solid surface to which sufficient amounts of cytochrome c aqueous solutions were further
added and the dried. Selective removal of polystyrene template by nonpolar solvent resulted in formation of nanoporous films of cytochrome c. Electrochemical investigation of the prepared film revealed their high stability. The fabricated films can be easily subjected to QCM-based gas sensing, exhibiting higher sensitivity to toxic acidic vapors.

B. Dynamic structural transformation to hierarchic material

In addition to the conventional self-assembling processes, dynamic shape-shifts of self-assembled structures have been also considered to prepare the functional materials with hierarchic nanoarchitectures. Leong and co-workers fabricated hierarchic layered materials through self-assembly of two-dimensional MoS$_2$ nanosheets and DNA strands and their dynamic behaviors of assembly/disassembly for cancer therapy. DNA oligonucleotides with thiol group at their terminal were first immobilized on to the MoS$_2$ nanosheets through binding at sulfur atom defects. The formed hybrid nanosheets were further assembled into layer-by-layer structural motif upon bridging the DNA strands with the linker aptamer. Drugs for therapy can be entrapped within the architected layered materials with protection from external disturbances. Because the aptamer has strong affinity to ATP molecules, the layered materials are disassembled under ATP-rich environments such as cancer cells. Dynamic assembly and disassembly depending on the presence of ATP can be converted to more advanced functions of drug protection and selective drug release for cancer apoptosis.

Zhang et al. reported structure dynamic transformation from Prussian blue cubes to their monocristalline nanoframes through the selective etching process. Cubic-shaped NiFe($\text{II}$) Prussian blue analogies were self-assembled and subjected to aqueous HCl incubation under ambient conditions. Because etching occurs preferentially at their face rather than edge regions, the normal cubes were first changed to concave cubes and then eventually to nanoframes. The presence of crystalline defect at the surface of cube faces rather than edges and corners would be cause of the observed site-selective etching. The remaining nanoframes have monocristalline nature and exhibited enhanced electrochemical performances such as an excellent rate performance with stable cycling on sodium/lithium ions insertion and extraction. The dynamic shape conversion resulted in several structural features such as improved crystallinity, good accessibility of molecules and ions, and enhanced surface-to-volume ratios, which are mostly advantageous in many applications.

Fabrication of hierarchic structures, rod-on-cube, was demonstrated by Shrestha and co-workers through self-assembly of C$_{70}$ molecules at the liquid-liquid interface and post solvent treatments (Fig. 6). Self-assembled precipitation of C$_{70}$ molecules at tert-butyl alcohol and the mesitylene interface provide cubic shaped materials of C$_{70}$. The architectured cubic structures were converted into hierarchic rod-on-cube materials simply by washing with isopropanol. Partial dissolution of C$_{70}$ molecules at the cube surface and conversion into one-dimensional small rods resulted growth of nanorods basically perpendicular to the faces of the cubes. In addition, every nanorod has mesoporous structures, and thus the entire rod-on-cube materials have an integrated hierarchic structure motif. The hierarchic natures of the architectured materials are advantageous for sensing of aromatic vapors with favorable $\pi-\pi$ interaction, high surface area feature, and facile diffusion. The rod-on-cube C$_{70}$ materials also showed enhanced performance in energy storage capacity.

A similar but more dynamic liquid-liquid precipitation process can give hole-in-cube structures, too. In this case, a mesitylene solution was dynamically added to tert-butyl alcohol followed by 24 h incubation at 25 °C, resulting in hierarchic assembly of hole-in-cube structures of C$_{70}$. At the fabricated hole-in-cube materials, one hole was isolated at center of every face of cube. These holes can be intentionally closed by forming a thin sheet on the hole upon addition of extra C$_{70}$ molecules, and then the holes can be intentionally re-opened by the irradiation of electron beam. The holes are at micrometer-size and are capable of trapping microscopic objects with certain selectivity. For example, graphitized carbon microspheres are more selectively entrapped into holes at the surfaces of cubes rather than microspheres of conventional polymer resins. This microscopic discrimination would be caused by the favorable $\pi-\pi$ interaction between the holes with the inner C$_{70}$ surface and graphitic surface nature of the former microsphere. Therefore, the nanoarchitected hole-in-cube structures would be useful for removal of toxic particles such as PM 2.5 from atmosphere.

Spontaneous shape-shifts as analogous with embryonic development were also demonstrated at self-assembly of the liquid-liquid interface using two kinds of fullerene (C$_{60}$) derivatives, pentakis(phenyl)fullerene and pentakis-(4-dodecylphenyl)fullerene. Self-assembly of the mixture of these derivatives at interfaces between toluene and isopropyl alcohol resulted in formation of microspheres with phase-separated patch domains of pentakis-(4-dodecylphenyl)fullerene. Changes of medium from the two-phase system to homogeneous mixture induced growth of one-dimensional tubes of pentakis-(4-dodecylphenyl)fullerene from the patch domains. As total processes, conversion from egglike assembly to tadpolelike assembly can be mimicked only through the self-assembly of two simple organic compounds. This process can be
named as supramolecular differentiation. A number of tales from a single sphere can be also controlled by the initial incubation time as time-programmed self-assembly. This discovery is useful to architect anisotropic and/or integrated structures of self-assembled materials. In addition, they may regenerate artificial differentiations without using commands from DNA.

C. Material preparation and function with dynamic flow at interfacial media

As exemplified above, dynamic processes at interfacial media are sometimes advantageous for fabrication of hierarchic self-assembled structures and spatiotemporal shape shifts of self-assembled materials. Similarly, macroscopic visible-size motions at interfaces sometimes have crucial roles in materials fabrications and controls of molecular functions. In this section, some recent examples on motion-controlled materials fabrication and control of molecular machines at interfacial media are introduced.

Use of the Langmuir-Blodgett (LB) method at gas-liquid interfaces, mainly air-water interface, is not limited to fabrication of monolayers of amphiphilic molecules and their multilayers. This strategy is often used to make aligned assemblies of various nanomaterials. Introduction of rotational flow at water surface enables us to prepare well-aligned two-dimensional assemblies of one-dimensional carbon nanowiskers, which were used as scaffolds for regulation of living cell assemblies and differentiation. This novel methodology using liquid flow at liquid surfaces is called the vortex LB method. Recently, this vortex LB technique was utilized for bottom-up synthesis of two-dimensional carbon films from molecularly engineered carbon nanoring, 9,9′,10,10′-tetra-butoxy-cyclo[6]-paraphenylene-[2]-3,6-phenanthrenylene (Fig. 7). Two-dimensional molecular nanosheet was first self-assembled at the air-water interface with the aid of flows with a vortex motion of subphase. Transferred assembled nanosheet was further converted to two-dimensional carbon nanosheets though carbonization under inert gas flow. While homogeneous two-dimensional morphology with nanometer-level thickness was retained after the carbonization processes, conductivity of the film was drastically increased upon film graphitization. Doping of heteroatoms such as nitrogen can be done easily by mixing additional component in these bottom-up fabrication processes. For example, addition of small amount of pyridine to the carbon nanoring molecules resulted in efficient nitrogen doping to the carbon nanosheet after carbonization accompanying with a further increase in the film conductivity. Large-scale production of two-dimensional carbon nanofilms with tunable conductivity would be useful for catalysts and energy storage applications. The demonstrated simple process may satisfy this practical demand.

This strategy to optimize fabrication of nanomaterials is useful to design and fabricate nanoarchitecture and microarchitecture with well-defined shapes through self-assembly of DNA origami pieces with programmed sequences. Further assembly of DNA origami pieces into hierarchic and superior structures have to be considered. As demonstrated by Yonamine et al., dynamic motional assembly at the air-water interface was used for one-dimensional supramolecular polymerization of rectangle DNA origami. In order to float the rectangle DNA origami pieces on water, the DNA origami pieces were first complexed with cationic dialkyl lipid (dioctadecyldimethylammonium bromide) molecules through electrostatic interaction. The lipid-complexed DNA origami pieces can be dissolved in organic solvent to form a homogeneous solution, which upon spreading at the air-water interface forms monolayer structures of the DNA origami. Although individual rectangle shape of the DNA origami was preserved just after spreading, repeating mechanical processes of the monolayer compression and expansion induced anisotropic supramolecular polymerization resulting in the formation of one-dimensional belt-shaped structures that kept thickness and width of the unit DNA rectangle but extended to one direction with a high aspect ratio. In the DNA rectangle structure, DNA hybridization is completed at two long sides, but single-stranded loops remain at two short sides. Dynamic motions probably induce nonspecific hybridization of single-stranded DNA loops at neighboring DNA origami pieces and anisotropic supramolecular polymerization through hydrogen bonding between short sides of DNA rectangle pieces.

As seen in the above-mentioned example, hydrogen bonding capability is known to be highly enhanced at the air-water interface as compared with bulk water media. Therefore, the air-water interface is an effective medium for molecular recognition where artificial molecular receptors are embedded to recognize aqueous biomolecules. In addition, dynamic compression of molecular receptor monolayers can be used for fine tuning of receptor conformations to optimize recognition capabilities. For example, tuning of molecular twisting of the molecular receptor, cholesterol-armed cyclen having 1,4,7,10-tetraazacyclododecane core and four cholesteric side arms, was demonstrated by lateral mechanical compression of the monolayer of this receptor at the air-water interface. Enanti-selective binding of aqueous amino acids can be regulated by surface pressures. Mechanical tuning of the molecular receptor, cholesterol-substituted triazacyclonane, at the air-water interface can find the optimized condition for the discrimination of thymine derivative and uracil derivative. This strategy to optimize recognition capability from numerous conformational candidates by

FIG. 7. Bottom-up synthesis of two-dimensional carbon films from molecularly engineered carbon nanoring, 9,9′,10,10′-tetra-butoxy-cyclo[6]-paraphenylene-[2]-3,6-phenanthrenylene with the aid of flows with a vortex motion at the water surface followed by calcination.
mechanical tuning of receptor conformations can be recognized as a novel mode for molecular recognition after (i) the first generation with consideration of one stable structure and (ii) the second generation with structure switching between a couple of stable states by external stimuli. The dynamic interface such as the air-water interface has two extreme dimensional sizes, infinite macroscopic size in the lateral direction and the nanoscopic level confinement along the thickness direction. Therefore, macroscopic motions such as human hand motions can be coupled with nanoscopic functions such as molecular machine functions at dynamic interfacial media. For example, steroid cyclophane molecular machine, 1,6,20,25-tetraaza-[6.1.6.1]-paracyclophane cyclic molecule connected to four cholic acid boards through a flexible L-lysine arm, as a guest-catcher-type molecular machine was embedded at the air-water interface as its monolayer (Fig. 8). Mechanical macroscopic deformations, compression and expansion, on the monolayer induced the conformational changes of steroid cyclophane molecular machines between cavity and flat conformers accompanying with guest capture and release, respectively. Similar mechanical controls of molecular machines using molecular pliers, molecular rotors, and molecular flappers have also been demonstrated.

As demonstrated in several examples above, dynamic motions such as liquid flows and mechanical deformations at interfaces are useful for fabrication of two-dimensional materials, organization of DNA origamis, tuning of molecular receptors, and controls of molecular machines. Interfaces as dynamic two-dimensional media can couple macroscopic motions and nanoscopic molecular functions, and therefore controls of molecular systems and materials by mechanical motions become possible.

IV. FUTURE OUTLOOK

In this short perspective article, recent trends on materials nanoarchitectonics upon supramolecular self-assembly are first overviewed. Important key terms, dynamic natures, dimensional controls, and interfacial processes, were successfully extracted by these overview processes. These key features have been well used in recent efforts for conversion from self-assembled structures into nanostructured materials. In addition, the dynamic processes at the interface can be connected with forefront functions such as tuning of molecular receptors and mechanical controls. These three key terms, dynamic natures, dimensional controls, and interfacial processes, are regarded as crucial factors for fabrication of functional materials and controls of nanosystems (Fig. 9). These nanoarchitectonic strategies can be also coupled with other related approaches based on molecular architectonics and advanced molecular designs.

![FIG. 8. Control of motions of steroid cyclophane molecular machine at the air-water interface of mechanical macroscopic deformations, compression, and expansion.](image_url)

![FIG. 9. Key factors in fabrication of functional materials and controls of nanosystems upon nanoarchitectonics concept: dynamic natures, dimensional controls, and interfacial processes.](image_url)
As a future perspective, these concepts are applied for the control of more advanced and complicated systems such as biosystems including living cells. For example, Li and co-workers developed dimensional controls of the self-assembly of biomolecules, diphenylalanine dipeptide. Upon the one-step rapid evaporation process, Christmas-tree-like tubular structures with large numbers of branches could be nanoarchitected. Because crystalline tubular structures have high optical waveguide capabilities, light harvesting behaviors with collecting lights at branch points were demonstrated. Such biomolecular nanoarchitectures would be useful for the artificial photosynthesis. Cell cultures have been investigated both at the surface of rigid aligned fullerene nanowhiskers and even at the liquid-liquid interface. For example, culture of human mesenchymal stem cells at the liquid interface between an aqueous culture medium and a perfluorocarbon solvent revealed the importance of monomolecular protein nanosheet spontaneously formed at the liquid interface. Tailoring of the mechanical dynamic properties of the self-assembled protein monolayer is key for cell spreading and possible differentiation. Such novel cell culture techniques on the basis of interfacial dynamics would be very useful for cell engineering and regenerative therapies.

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