Soft materials nanoarchitectonics at interfaces: molecular assembly, nanomaterial synthesis, and life control

Journal:	*Molecular Systems Design & Engineering*
Manuscript ID	ME-REV-11-2018-000094.R1
Article Type:	Review Article
Date Submitted by the Author:	03-Jan-2019
Complete List of Authors:	Ariga, Katsuhiko; National Institute for Materials Science, World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA) Jia, Xiaofang; National Institute for Materials Science International Center for Materials Nanoarchitectonics Shrestha, Lok Kumar; National Institute for Materials Science (NIMS), WPI Center for Materials Nanoarchitectonics (MANA)

Design, System, Application Statement

limitation of motional freedom by reducing system dimension from three-dimension to two-dimension is advantageous in several cases. Therefore, this feature is useful for soft materials that have high possibilities of changes in their conformations, shapes, motions, orientations and arrangements. Nanoarchitectonics at surface media such as solid surfaces, air–water interfaces, and liquid–liquid interfaces would be attractive strategy for preparation of functional materials with soft material components. For these strategies, molecules and materials are designed to promote specific interactions such as hydrogen bonding at interfacial environments. The presented examples are classified according to the following processes: (i) from molecules to two-dimensional materials systems at the air–water interface; (ii) from interfacial assembly to hierarchical nanostructures with layer–by–layer assembly; (iii) from interfacial assembly to hierarchical nanostructures at liquid–liquid interface: (iv) from materials system to life control at interface. These examples strikingly demonstrate utilities of the soft materials nanoarchitectonics at interfaces in various applications such as sensing and cell culture as well as forefront applications of molecular machine controls.

Molecular Systems Design & Engineering

REVIEW

Soft materials nanoarchitectonics at interfaces: molecular assembly, nanomaterial synthesis, and life control

Katsuhiko Ariga,*[a,b] Xiaofang Jia[a] and Lok Kumar Shrestha[a]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

A new conceptual paradigm to combine nanotechnology and the other research disciplines called “nanoarchitectonics” has been established. Nanoarchitectonics can be achieved with contributions of atomic/molecular level manipulation, chemical synthesis/modification, self-organization/self-assembly, field-controlled arrangement, material fabrication, bio-related techniques together with advanced knowledge and skills in nanoscience and nanotechnology. Especially, dynamic nature of the nanoarchitectonics concept accord with soft materials functionalization. Therefore, the nanoarchitectonics concept provides rational strategies to create functional materials with deep relations with molecular system designs that are especially useful for the developments of novel functions of soft materials. In this review article, recent research efforts on soft materials nanoarchitectonics at interfacial media are mainly focused. The presented examples are classified according to the following processes: (i) from molecules to two-dimensional material systems at the air–water interface; (ii) from interfacial assembly to hierarchical nanostructures with layer–by–layer assembly; (iii) from interfacial assembly to hierarchical nanostructures at liquid–liquid interface; (iv) from material systems to life control at interface.

1. Introduction

Preparations and fabrications of functional materials and systems are central issues in the developments of multiple functions and applications including materials synthesis and production,[1] sensing and separation,[2] environmental matters,[3] energy conversion and storages,[4] advanced devices,[5] and biological and biomedical applications.[6] With the current developments of nanoscience and nanotechnology, synthesis of functional materials has been done with higher contributions of designs of nano-scale materials. Especially, rational construction of functional structures is widely performed using hard inorganic nanomaterials,[7] because the latter components have less possibilities in structural uncertainties and fluctuations. In contrast, fabrications of materials with soft and flexible components *i.e.* soft materials syntheses often include uncontrollable aspects in materials construction, although such soft natures of materials are in turn advantageous for dynamic functions such as stimuli-responsive properties.[8] Soft materials syntheses with nanoscale units often require contributions of the other scientific disciplines including organic syntheses,[9] supramolecular chemistry with self-assembly/self-organization,[10] templates syntheses,[11] and bio-nanotechnologies such as DNA origami technology,[12] in addition to well-known nanotechnological fabrications.[13] Therefore, a new conceptual paradigm to combine nanotechnology and these research disciplines has to be established. A novel concept, “nanoarchitectonics”,[14] has been proposed as possibly the most appropriate for this demand.

In the transition period from the 20th century to the 21st century, necessity of the architectonics concept with nanoscale component materials was realized.[15] In 1999, an article entitled “Architectonic Quantum Dot Solids”, was published by Heath and co-workers.[16] The exact term, nanoarchitectonics, was first used in the conference title: “the 1st International Symposium on Nanoarchitectonics Using Suprainteractions” in Tsukuba, by Masakazu Aono in Japan in 2000.[17] It would be the first example to use the term of nanoarchitectonics in this meaning at scientific communities. In 2001, the National Institute of Advanced Industrial Science and Technology initiated a research centre of Interfacial Nanoarchitectonics with leader of Toshimi Shimizu. A research center named, Functional Engineered Nano Architectonics was established at UCLA in 2013. The first scientific paper with term of nanoarchitectonics, “Welding, organizing, and planting organic molecules on substrate surfaces - Promising approaches towards nanoarchitectonics from the bottom up”, was published by Stefan Hecht in 2003.[18] In 2007, Masakazu Aono started to direct a research center, World Premier International Research Center for Materials Nanoarchitectonics (WPI-MANA) in Tsukuba, Japan.

Nanoarchitectonics can be achieved with contributions of atomic/molecular level manipulation, chemical synthesis/modification, self-organization/self-assembly, field-controlled arrangement, material fabrication, bio-related techniques together with advanced knowledge and skills in nanoscience and nanotechnology (Figure 1).[19] The nanoarchitectonics concept is very general and is applicable to a wide range of scientific and technological disciplines from

---

[a] *WPI Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan, E-mail: ARIGA.Katsuhiko@nims.go.jp.*

[b] *Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan.*

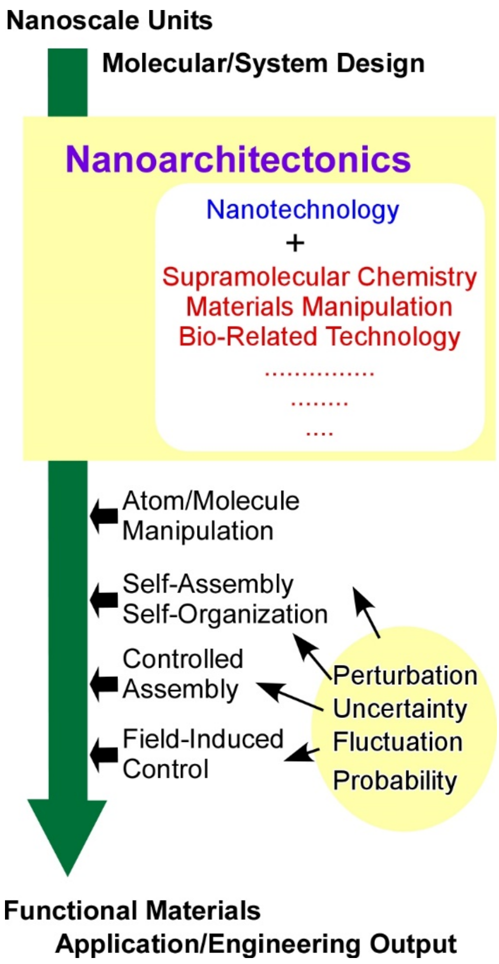

Figure 1 Outline of the nanoarchitectonics concept with related research fields, actions, and factors.

molecular system design to engineering including preparation of functional materials,[20] fabrication of advanced supramolecular assemblies,[21] target detection and sensors,[22] the energy-related applications (batteries and capacitors),[23] ecological and environmental issues,[24] catalysts,[25] devices,[26] and biological/biomedical applications.[27]

Dynamic natures of the nanoarchitectonics concept especially accord with soft materials functionalization. One of the distinct features of the nanoarchitectonics concept would be harmonization of processes and working principles.[28] Effective size regions of the nanoarchitectonics range from nanometers to micrometers in which quantum effects, static distributions, and thermal fluctuations may be uncontrollably involved in the architecting processes together with unexpected mutual interactions between components. Therefore, balanced harmonization between various factors becomes practically important than perfect and precise control of possible factors, the latter of which may be virtually impossible. In many cases, the nanoarchitectonics process is supposed to dynamically manage various interactions possibly with their unpredictable uncertainties in balanced harmonization, which is an important feature for the soft materials fabrications.

Because the nanoarchitectonics processes have to harmonize rather complicated interactions, limitation of the motional freedom by reducing system dimension from three-dimension to two-dimension is advantageous in several cases.[29] Especially, this feature is useful for soft materials that have high possibilities of changes in their conformations, shapes, motions, orientations and arrangements. Nanoarchitectonics at surface media such as solid surfaces, air–water interfaces, and liquid–liquid interfaces would be attractive strategy for the preparation of functional materials with soft material components. Immobilization of components on solid surface would provide opportunity for the high-resolution observation of nanoarchitectonics processes. In contrast, highly dynamic and flexible natures of liquid interfaces provide certain freedom of component diffusion, rearrangements, and mixing, but two-dimensional (2D) confined natures of the interfacial media prevent the components and architected materials from limitlessly dispersing. In addition, molecular interactions at interfacial media with discontinuous changes of dielectric nature are highly modulated, resulting in efficient and direction-specific molecular association.[30]

In this review article, recent research efforts on the soft materials nanoarchitectonics at interfacial media are exemplified. These examples are classified according to the following processes: (i) from molecules to 2D material systems at the air–water interface; (ii) from interfacial assembly to hierarchical nanostructures with layer–by–layer (LbL) assembly; (iii) from interfacial assembly to hierarchic nanostructures at liquid–liquid interface: (iv) from materials system to life control at interface. Finally, future technology such as control of molecular machines and nanocars at interfacial media are also discussed in conclusive section.

2. From molecules to 2D material systems at the air–water interface

Dynamic interfaces such as the air–water interface are appropriate media for softly assembling molecules to architect functional materials in ultrathin film form and 2D molecular patterns. At the air–water interface, component molecules preserve their high motional freedom at heterogeneous 2D environment between two phases with totally different dielectric constants. Therefore, the component molecules possess high opportunities of free contact in both lateral and vertical directions avoiding limitless dispersion in the bulk phase.

Especially, monolayer films at the air–water interface provide rational encountering points between synthetic molecules (monolayer) and biomolecules from aqueous subphase.[31] In biological systems, molecular recognition between target signal molecules and receptor biomolecules, specific hybridization of nucleic acid strands, and selection of substrates by enzymes actually happen at aqueous interfacial media such as cell membrane surfaces, macromolecular interfaces, and pockets of protein insides. The air–water interface works as an appropriate medium as a model of aqueous bio-interfaces for the molecular recognition and

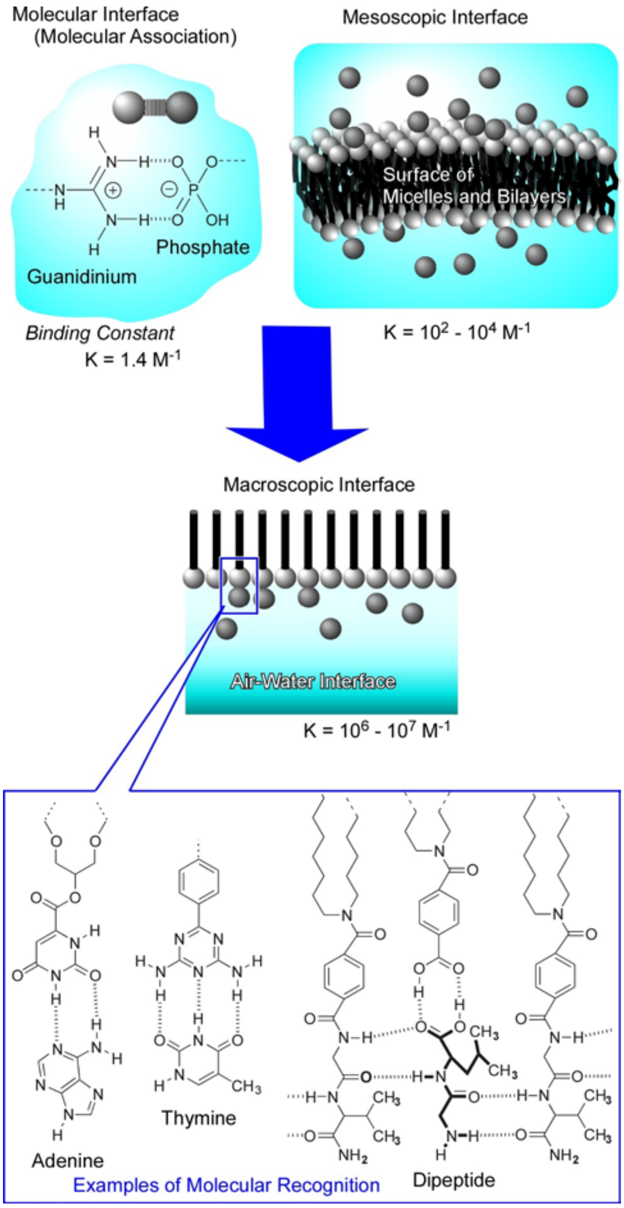

Figure 2 Molecular recognition at the air–water interface: striking enhancement of binding constant and rich variety of guest selection with examples of recognition motifs.

assembly. Striking enhancement of molecular interaction at the air–water interface was proved both experimentally and theoretically (Figure 2).[32] While binding constants of electrostatic hydrogen-bonding pair between guanidinium and phosphate were assigned to 1.4 M^{-1} at molecular dispersion in aqueous phase[33] and 10^2–10^4 M^{-1} in aqueous mesoscopic interfaces of micelles and lipid bilayers,[34] the corresponding constants are enhanced to 10^6–10^7 M^{-1} at the air–water interface.[35] The experimentally observed striking enhancement of molecular recognition efficiency can be also proved by quantum chemical calculations at interfacial media between low dielectric phase (lipid) and high dielectric phase (water).[36] Contribution of favourable characteristics for electrostatic hydrogen-bonding at low dielectric phase is significant at less-disturbed aqueous interface. According to these discoveries, efficient molecular recognitions for various biomolecules including sugars,[37] amino acids,[38] nucleotides,[39] nucleic acid bases,[40] and peptides[41] have been accomplished at the air–water interface.

These enhanced natures of molecular interactions at the air–water interface are advantageous for the preparation of 2D pattern structures in molecular-level precision through molecular assemblies within 2D medium with the aid of aqueous components. This methodology, so-called 2D molecular patterning,[42] utilizes aqueous template molecules with multiple binding sites to make defined arrangement of amphiphiles through specific molecular recognition at the air–water interface (Figure 3). Specific binding of an aqueous dicarboxylate template to guanidinium amphiphiles resulted in a regular 2D molecular pattern upon crystal lattice depending on lengths of spacer between two carboxylate groups in the template.[43] Regular patterns were prepared through formation of supramolecular polymers of dialkylmelamine amphiphiles and aqueous barbituric acid molecules.[44] Binding of one aqueous flavin adenine dinucleotide template to two guanidinium amphiphiles and one orotate amphiphile can create 2D molecular patterns with sub-nanometer level regular structures.[45]

Importance of regulation of molecular arrangements within 2D environments is well recognized in lipid raft formation at biological cell membranes, which is deeply related to various biological functions. However, driving forces for the formation of lipid rafts have not been fully understood. In a recent review by Mukai and Regen,[46] they have detailedly investigated the lipid raft formation with the nearest-neighbour recognition concept and suggested important roles of polyunsaturated phospholipids in the lipid raft formation.

As raft-like nano-domain formation by artificially designed molecules, 2D nanoarchitectonics with fluorocarbon-hydrocarbon diblock molecules upon intrinsic immiscible nature between fluorocarbon and hydrocarbon are introduced in a recent review article by Krafft and co-workers.[47] When these diblock molecules spread at the air–water interface, circular mesoscopic nano-domains were unusually formed even at zero surface pressure. Further compression of the monolayer of fluorocarbon-hydrocarbon diblock molecules resulted in the formation of regular hexagonal arrays. Oishi and co-workers reported controlled formation of regular domain within the mixed monolayer of fluorocarbon carboxylic acid and hydrocarbon guanidinium on the basis of balances of repulsive interaction between fluorocarbon and hydrocarbon and attractive force between carboxylate and guanidinium (Figure 4).[48] Their domain sizes and shapes can be controlled from the nanometer to the micrometer scales by various external factors including temperature, pH, pressure, composition, and ionic strength.

Regularly assembled molecules at interfacial media often show interesting properties because they possibly have unique orientation, anisotropy, and aggregation. Seki summarized motions of photo-active molecules and macromolecules in their

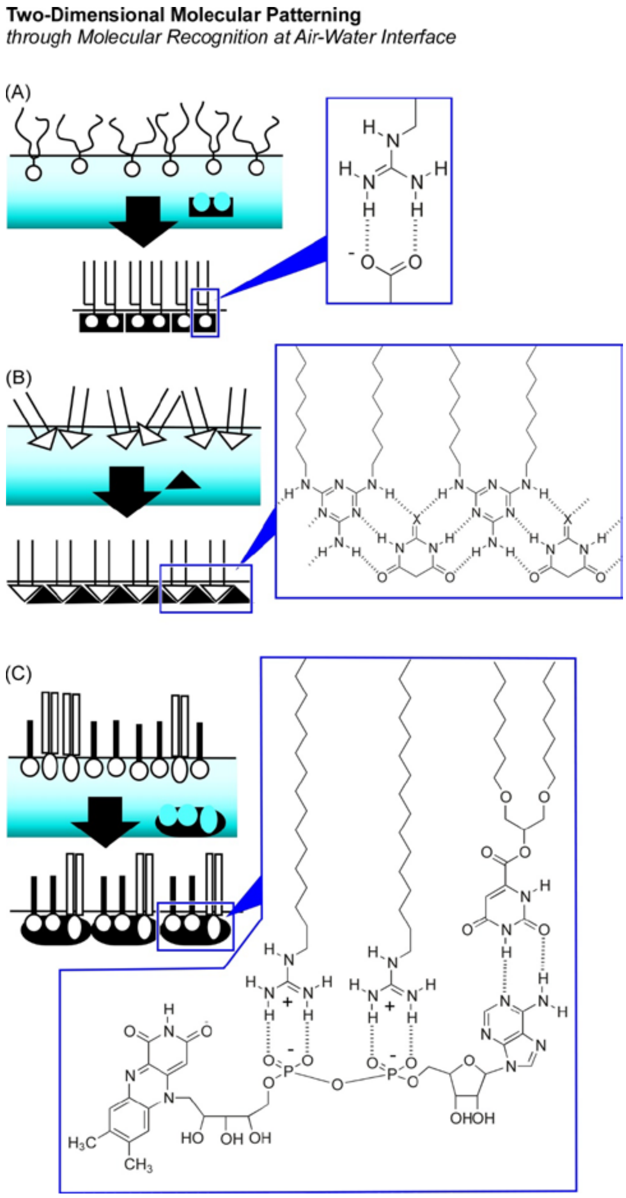

Figure 3 Strategies for 2D molecular patterning: (A) crystalline lattice control through interaction between dicarboxylate template and guanidinium amphiphiles; (B) regular patterns formation through formation of supramolecular polymers of dialkylmelamine amphiphiles and aqueous barbituric acid template; (C) pattern formation based on binding of one aqueous flavin adenine dinucleotide template to two guanidinium amphiphiles and one orotate amphiphile.

assemblies at interfaces in his recent review article.[49] Spatial-temporal motional control of soft materials in sub-micrometer level precision can be accomplished with sufficient repeatability and durability. Conversion of photonic energies to mechanical functions would open a new paradigm of soft materials nanoarchitectonics.

Sakakibara et al. demonstrated regulation of photo-energy conversion and transfer processes of the assembled structures of oligo(*p*-phenylenevinylene)-derived π-gelator.[50] This molecule assembled into supramolecular fibers of entangled network upon drop-casting its solution on a solid surface

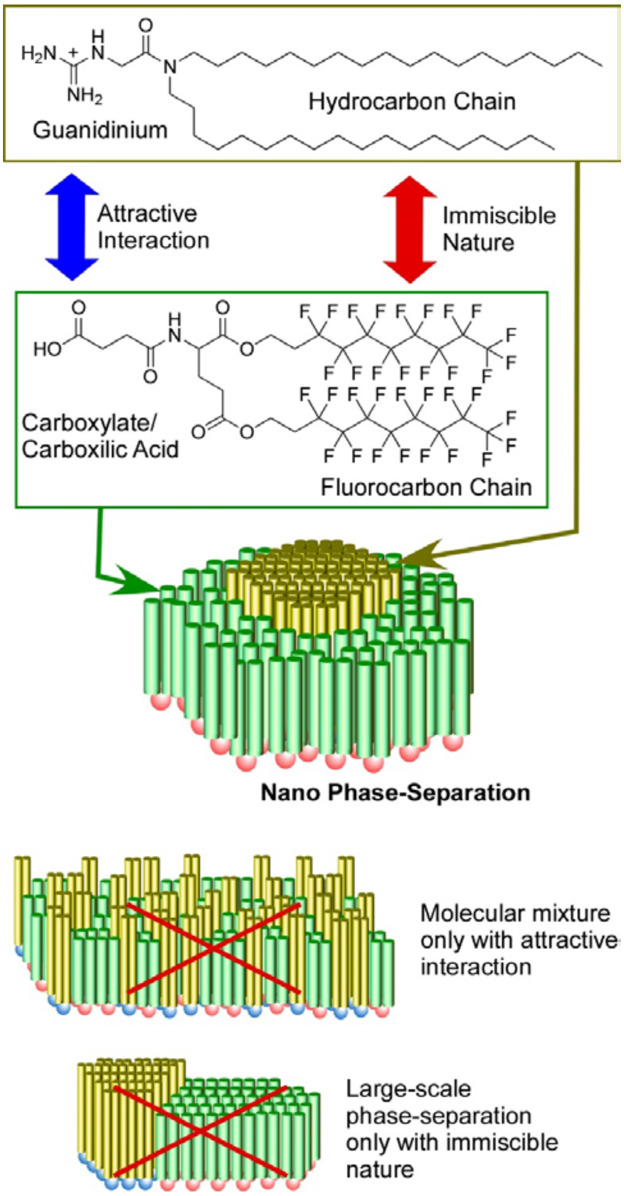

Figure 4 Regular domain formation upon nano phase-separation in mixed monolayer of fluorocarbon carboxylic acid and hydrocarbon guanidinium on the basis of balances of repulsive interaction between fluorocarbon and hydrocarbon and attractive force between carboxylate and guanidinium.

(conventional technique). In the formed network fibers, oligo(*p*-phenylenevinylene) segments are arranged perpendicularly to the long axis of the fiber. The orientation is favorable for the long-range excitation energy transfer. On the other hand, spreading the same molecule at the air–water interface creates aligned nanorods in which the oligo(*p*-phenylenevinylene) segments are mainly orientated in parallel to the long axis of the nanorods. In the latter case, fluorescence enhancement would be significantly induced, which is appropriate for the charge transport.

Molecular recognition at the air–water interface is not limited to complex formation between separate component species. Continuous formation of molecular recondition

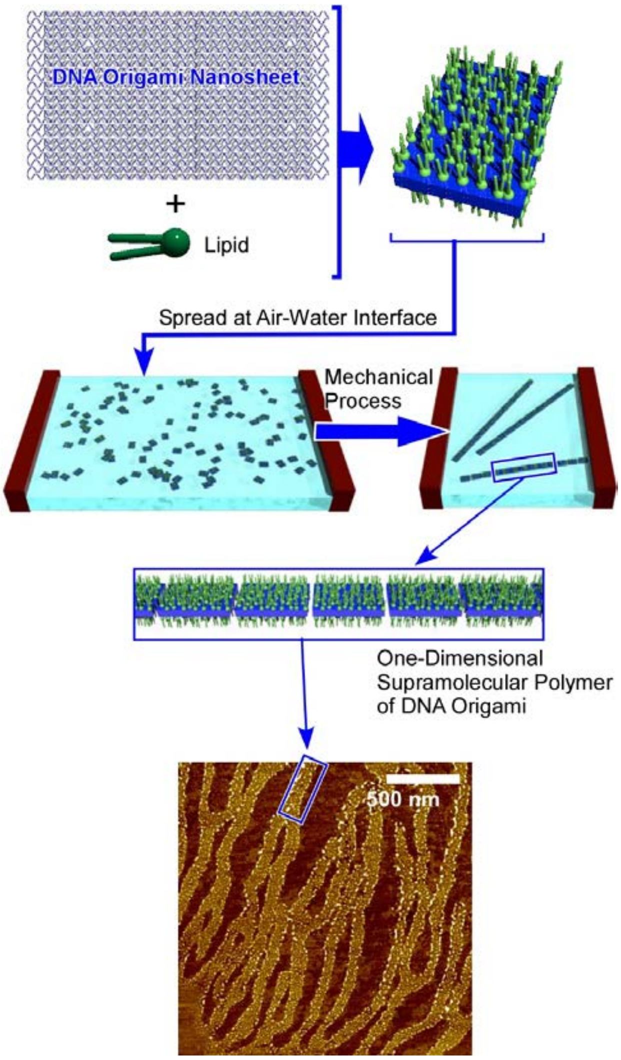

Figure 5 Formation of Langmuir films and LB films of DNA origami with formation one-dimensional supramolecular polymerization of the DNA origami upon 2D mechanical actions.

structures resulted in two-dimensionally developed materials. As discussed in the recent review article by Sakamoto,[51] this strategy is appropriate for the preparation of low-dimensional materials through well-defined molecular interaction such as coordination and hydrogen bonding. In fact, interfacial environments such as the air–water interface provide opportunities to form 2D nanosheets of coordination polymers and metal–organic frameworks. Similarly, hydrogen bonding-based supramolecular polymerization between amphiphilic melamine and barbituric acid to form linear polymer–like extended one-dimensional structure was accomplished on the basis of enhanced efficiency of hydrogen bonding at the air–water interface.[44,52]

Supramolecular polymerization of DNA origami pieces at the air–water interface was recently reported by Yonamine et al. who first demonstrated formation of Langmuir films and Langmuir–Blodgett (LB) films of DNA origami (Figure 5).[53] The DNA origami pieces used in this research possessed rectangular shape (90 nm × 65 nm in dimension), which was complexed with cationic lipid to give sufficient solubility in organic solvents such as chloroform. A chloroform solution of the rectangular DNA origami was spread at the air-water interface to form its Langmuir monolayer. Although the DNA origami pieces kept their rectangle shape at the air–water interface, repeated cycles of lateral mechanical compression and expansion of the DNA origami monolayer activated motions of the DNA origami in 2D plane. This dynamic process induced one-dimensional supramolecular polymerization of the DNA origami pieces through hydrogen bond formation at umpired DNA strands at two opposite sides of the rectangle piece. While width and thickness of the formed belt-shaped supramolecular polymers, their lengths were increased to 130 nm, 680 nm and 2240 nm after the first, second and third compression, respectively. Yonamine et al. also demonstrated lipid-fuelled transfer of DNA wheels at the solid interface from hydrophilic surface to hydrophobic surface.[54] DNA wheels are basically hydrophilic, but addition of lipid to the system makes them hydrophobic, resulting in 2D transfer of the DNA wheels. This transfer is made through the solution space accompanied with a flip-flop motion.

Materialization of assembled structures at the air–water interface leads to bottom-up synthesis as recently demonstrated by Mori et al. who successfully prepared carbon nanosheets through carbonization of two-dimensionally assembled carbon nanorings at the air–water interface with vortex flow.[55] In this approach, anisotropic carbon nanoring molecule, 9,9’,10,10’-tetra-butoxy-cyclo[6]-paraphenylene[2]-3,6-phenanthrenylene, was spread onto water surface with a constant vortex flow (Figure 6). Self-assembling process with dynamic motion resulted in the formation of molecular nanosheets. Heat-treatment of the assembled nanosheets under a constant inert gas flow resulted in ultrathin uniform carbon nanosheet with nanopore structures maintaining the original 2D morphology of the molecular assembly but with sufficient increase of electric conductivity. Fabrication of nitrogen-doped carbon nanosheets were also prepared by simply mixing pyridine in the original monolayer components. The nitrogen-doped carbon nanosheets have further increased electrical conductivity and are also expected as a highly efficient catalyst for oxygen reduction reactions for high-performance fuel cells.

3. From interfacial assembly to hierarchic nanostructures with layer–by–layer assembly

Layered nanostructures are capable of immobilizing functional units within defined structures, which is useful for the preparation of materials with various functions.[56] For example, Oliveira Jr and co-workers used alternate layer structures monoclonal antibody and chitosan/gold nanoparticles as immuno-sensors for a biomarker of venous thromboembolism.[57] Ruiz-Hitzky et al. demonstrated sensing application for the detection of alkali ions by montmorillonite layered silicates with dimethylsila-14-crown-5 and dimethylsila-17-crown-6 macrocyclic polyethers.[58]

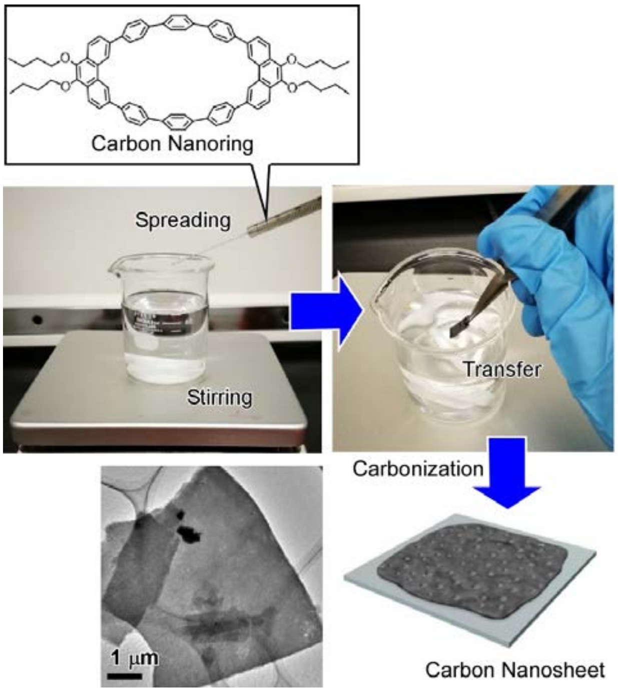

Figure 6 Preparation of carbon nanosheets through carbonization of two-dimensionally assembled carbon nanorings at the air–water interface with vortex flow (vortex LB method).

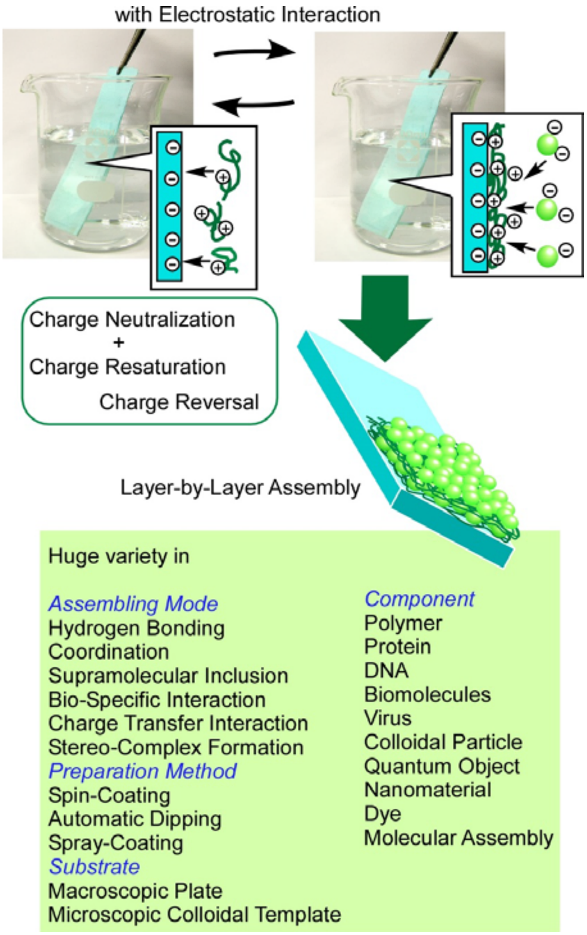

Figure 7 Outline of LbL assembly. Huge variety of component materials and assembling mechanisms can be involved.

In addition to the conventional functionalization of pre-formed layered structures, construction of layered structures from unit layers is also a powerful strategy to create functional materials with various components in defined structures. Conversion of interfacial assembly to hierarchical nanostructures can be accomplished through constructing unit monolayers into layered structures by appropriate methods such as LB method[59] and LbL assembly.[60] While the LB method provides well-packed precisely controlled thin films, less-organized flexible layered structures can be obtained from a wide range of materials by the LbL assembly as so-called fuzzy nano-assembly (Figure 7).[61] Basic mode of the LbL assembly is based on electrostatic interaction with charge neutralization and charge re-saturation, but the other interactions such as hydrogen bonding,[62] coordination,[63] supramolecular inclusion,[64] bio-specific interaction,[65] charge transfer interaction,[66] and stereo-complex formation[67] can also be used as driving force for the assembly. Procedures for the LbL assembly are very simple and can be done simply with beakers and tweezers in the most cases. Coupling with the other techniques such as spin-coating[68] and automatic dipping,[69] and spray-coating[70] are also possible. In addition, the LbL assembly is applicable to microscopic colloidal template for the formation of hollow microspheres.[71] The LbL assembly is one of the highly appropriate procedures in soft materials nanoarchitectonics in hierarchical layered motifs.

Various functions including electrochemical energy-related applications are expected from the 2D materials such as graphene and MoS_2 nanosheet.[72] Not limited to the typical applications, 2D materials can work as atomically flat structural components in the nanoarchitectonics structure fabrications. For example, 2D ultra-narrow gap filled with ionic liquid between highly π-conjugated nanosheets of reduced graphene oxide was fabricated with the aid of the LbL assembling technique.[73] In this approach, graphene oxide nanosheets were first dispersed and then converted to reduced graphene oxides in the presence of ionic liquid (imidazolium salts). The resulted reduced graphene oxide nanosheets were efficiently covered by imidazolium cations to keep them dispersed in water. The formed cationic complexes have alternate layered structures of graphene nanosheets and ultrathin ionic liquid phase, which were further nanoarchitected into LbL structures with anionic polyelectrolyte, poly(sodium styrenesulfonate), on an electrode surface of quartz crystal microbalance (QCM) sensor. Exposure of the surface modified QCM sensor to vapours of organic solvents resulted in the QCM frequency shifts upon adsorption of the tested organic vapours depending on their affinity to graphene–ionic liquid layered hybrids. Greater responses for vapour detection were obtained for aromatic molecules such as benzene and toluene. Sensitivity to aromatic benzene vapour with more than 10 times higher than that for aliphatic

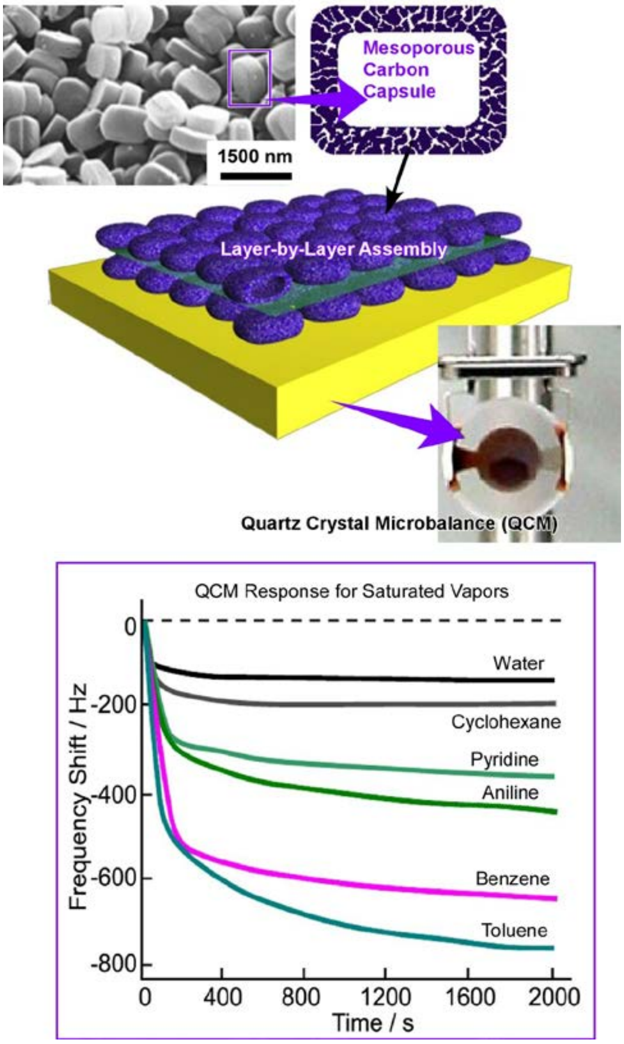

Figure 8 LbL assembly of mesoporous carbon capsules on a QCM sensor plate for sensing organic vapours with high sensitivity towards aromatic species.

cyclohexane was observed although these two molecules with similar molecular sizes, molecular weights, and vapour pressures. Liquid phase of imidazolium salts between graphene nanosheets would be highly π-electron rich 2D phase, where aromatic molecules would have higher partition coefficient.

Hierarchical nanoarchitectures can be fabricated through nanoarchitecting materials with internal nanostructures such as mesoporous carbon into layered motifs by the LbL method.[74] Standard mesoporous carbon, CMK-3, was first partially surface oxidized and then assembled into layered structures by the LbL assembly method together with polyelectrolytes, poly(diallyldimethlyammonium chloride) and poly(sodium stryrenesulfonate) on the QCM sensor plate. Detection of various tea components such as tannic acid, catechin and caffeine was investigated after immersing the QCM sensor with CMK-3 LbL films in water. Detection sensitivity to tannic acid well exceeded to those observed for catechin and caffeine because of size matching of the guest and nanopore inside. Interestingly, sigmoidal behaviors of adsorption amounts of tannic acids to CMK-3 LbL film as a function of concentration of tannic acid was observed. Highly cooperative adsorption of tannic acid within confined space of carbon nanochannels would be plausible reason of the higher sensitivity to tannic acid.

Higher level of hierarchical structures were nanoarchitected by LbL assembly of mesoporous carbon capsules with counterionic polyelectrolyte (Figure 8).[75] Mesoporous carbon capsules, with dimension of 1000 × 700 × 300 nm^3 and thickness of 35 nm with a uniform pore diameter distribution centered at 4.3 nm and a specific surface of 918 m^2 g^{-1}, were synthesized using zeolite crystals as template. After coated with charged surfactant, the mesoporous carbon capsules were assembled with appropriate polyelectrolytes in to LbL motif on the QCM sensor plates. Their sensor capabilities were examined by exposures of sensors to organic vapours, resulting in higher sensitivity to aromatic species on the basis of favourable π-π interaction. Further modifications of sensing affinities of these sensing systems can be done with impregnation of the second sensing components. Impregnation with lauric acids altered sensing affinity to aliphatic amine guests. In contrast, highly sensitive detection toward acetic acid vapour was obtained by doping of dodecyl amine as the second sensing components to the mesoporous capsules.

The similar hierarchical LbL structures can be fabricated with silica-based mesoporous capsules.[76] In the latter cases, the prepared hierarchical LbL structures can be used for materials delivery and drug delivery systems with unusual materials release profile. The hierarchical structural features lead to auto-modulated stimuli-free on-off release of molecules trapped within capsules.

Recently, Leong and co-workers reported the LbL assembly of DNA modified 2D MoS_2 nanosheets.[77] Good biocompatibility can be expected for the transition metal dichalcogenides MoS_2 nanosheets. The tagged DNA sequences were designed to be assembled only with complementary combinations, resulting in alternate layers of MoS_2 nanosheets and DNA. Desirable drugs such as doxorubicin can be loaded within the spaces between the sheets. Further, superstructures guided by a linker aptamer with recognition capabilities to ATP can be nanoarchitected. The drugs were safely shielded when the LbL structures were preserved. Encountering to ATP in cancer cells induces disassembly of the LbL structures to release drug molecules. According to the hierarchical design, the doxorubicin as an anticancer drug can be released under the highly metabolically active environment of cancer cells.

4. From interfacial assembly to hierarchical nanostructures at liquid–liquid interface

As demonstrated in recent various examples, hierarchical nanoarchitectonics of functional molecules and ionic species are capable of constructing various functional systems. Tanaka and co-workers proposed a method for the preparation of programmable hetero-atom ions using supramolecular arrays of porphyrin and phthalocyanine.[78] Haketa and Maeda recently

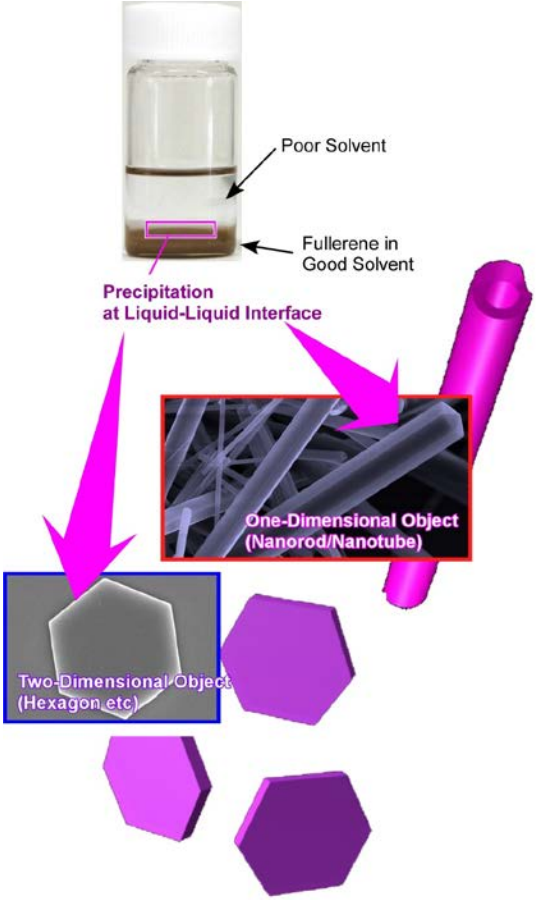

Figure 9 Various examples of nanoarchitectonics construction with fullerene (C_{60} and C_{70}) molecules by using liquid–liquid interfacial precipitation method.

reviewed methods to nanoarchitect dimension-regulated π-electronic ion-pairing assemblies,[79] which are useful for ion-responsive functional materials. Akamatsu et al. reported optical imaging of cesium ions on the basis of an optode membrane incorporating a calix[6]arene derivative and appropriate dye components.[80] The proposed system can be down-sized into ca. 100-nm-sized nanoparticles. These sensing systems can be utilized for detection of cesium ions at conventional environmental media including domestic water supplies and seawater.

As unique ion-related hierarchical assemblies, cubic-shaped three-dimensional crystals of organometallic heteronanostructure between C_{60} and silver ion, so called bucky cubes could be fabricated.[81] The bucky cube was precipitated at liquid–liquid interface between benzene or toluene solution of C_{60} and ethanolic silver(I) nitrate solution. Washing of the bucky cubes with low molecular weight aliphatic alcohols induced growth of needle-like crystals from the cube surface, resulting in needle-on-cube heterostructures.

As demonstrated in the last example, liquid–liquid interfaces are powerful media to form assembled and crystallized materials in regulated shapes (Figure 9).[82] Various examples of nanoarchitectonics construction with fullerene (C_{60} and C_{70}) molecules by liquid–liquid interfacial precipitation method have been reported as seen in pioneering examples of one-dimensionally grown C_{60} nanowhiskers and nanotubes reported by Miyazawa and co-workers.[83] At interface between good solvent and poor solvent for fullerenes, supersaturation induces formation of shape-defined nanostructures of fullerene molecules. Shapes, dimensions, and sizes of the formed fullerene nanoarchitectures can be controlled by selection of combinations of good and poor solvents together with the other physical parameters. Regular-shaped 2D nanostructures such as C_{60} hexagon nanosheets was formed.[84] Faint modification of the synthetic conditions in the liquid–liquid interfacial precipitation processes such as selection of poor solvents, fullerene concentrations, and volume rations of both the solvents resulted in the controlled nanoarchitectonics of fullerene crystals in one-, two-, and three-dimensional regular motifs.[85]

One of the successful fullerene nanoarchitectonics in three-dimensional motifs would be formation of cubic assemblies from pure C_{70} molecules.[86] These cubic objects can be formed using ultrasonic–agitated liquid–liquid interfacial precipitation between mesitylene solution of C_{70} and *tert*-butyl alcohol. The nanoarchitected C_{70} cubic assemblies were then converted into hierarchical structure of needles-on-cube nanoarchitectures simply upon exposure of the cubes to isopropyl alcohol at ambient condition. From surface faces of the cubes, rearrangements of C_{70} assemblies resulted in vertical growth of needles of C_{70} assemblies, which further possessed nanoporous structures. The hierarchical needles-on-cube nanoarchitectures with nanopores with high-surface-area natures are capable of high-performance sensing for toxic aromatic vapours. Enhanced interaction between sp^2-featured fullerene assembly with aromatic gases, high-contact probability, and easy diffusions of the guest gases would be causes of high-sensitive sensing. Like antenna of insects, the formed needles-on-cube nanoarchitectures could sense targets selectively and sensitively.

Another integrated three-dimensional nanoarchitectures of C_{70} assemblies are hole-in-cube assemblies of C_{70} molecules.[87] Formation of hole-in-cube assemblies, which as one open microscale hole on each face of the cubic assembly of C_{70}, was induced by mesitylene and *tert*-butyl alcohol treatment under appropriate level of agitating conditions. Manipulations of the open hole structures including intentional hole closures and re-opening were operative by addition of extra C_{70} molecules and local irradiations of electron beams, respectively. The created holes on the cube surfaces can trap microscopic objects selectively. Based on highly sp^2-nature of insides of holes, graphitic carbon microparticles was selectively trapped over polymer-resin microparticles with the similar size. Immobilization of hole-in-cube assemblies of C_{70} molecules on a QCM electrode would lead to fabrication of sensor system useful for the selective detection of micron-sized pollutant particles in environment with exhausted gas.

Time-programmed shape changes of fullerene assemblies like transformation from eggs to tadpoles were also demonstrated at liquid–liquid interfacial environments as defined by supramolecular differentiation (Figure 10).[88] This phenomenon has been realized through co-assembly process of

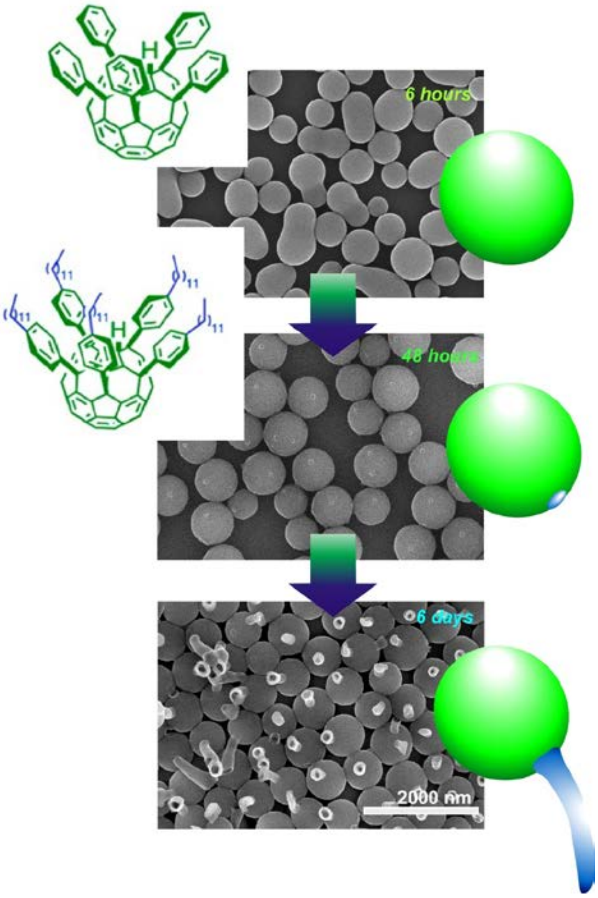

Figure 10 Time-programmed shape changes of fullerene assemblies like transformation from eggs to tadpoles were demonstrated at liquid–liquid interfacial environment as supramolecular differentiation.

fullerene derivatives with two-different substituents, alkyl arms and phenyl-attachments. Egg-like spherical assemblies were first formed. Sufficient incubation at appropriate liquid–liquid interfacial conditions induces local phase separation at the surface of the egg spheres. The formed phase-separated domains work as seeds for further growth of tube-like structures. After the programmed time interval under appropriate conditions, the tube-like structures start to grow like transformation from eggs to tadpoles. It would be surprising that non-living and non-DNA-including pure materials systems can imitate bio-like time-programmed shape transformation.

5. From materials system to life control at interface

Not limited to organic molecules and inorganic substances, nanoarchitectonics of biomolecules can also create advanced functions in both basic sciences and engineering applications.[89] Especially, bio-substances have intrinsic soft natures and thus can be important subject in soft materials nanoarchitectonics. Takahashi, Kamagata and co-workers proposed DNA garden strategy for the stretchable DNA arrays that can be used for single-molecule fluorescence imaging of DNA-binding proteins.[90] Desirable DNA nanoarchitectonics arrangements are made with micro-contact printing techniques to immobilize biotinylated bovine serum albumin to 2-methacryloyloxyethyl phosphorylcholine polymer on a coverslip. The subsequent tethering of neutravidin and biotinylated DNA achieved DNA gardening. The prepared DNA gardens can be used for single-molecule level observations on a tumor suppressor sliding along extended DNA chains and specification of restriction enzyme cleavage sites.

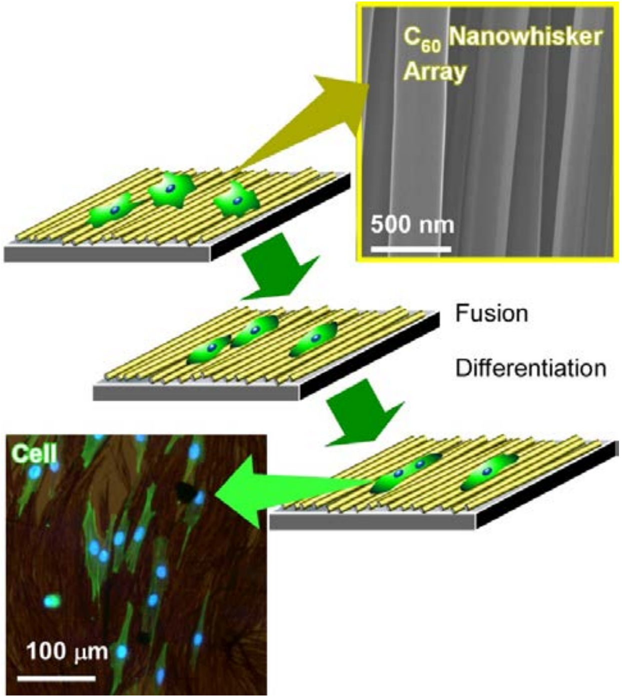

Figure 11 Promoted cell differentiations of C2C12 myoblast cells on interfacially nanoarchitected arrays of super-hard materials of fullerene nanowhiskers. Cell orientation and differentiation can be regulated.

He and Xu proposed a novel concept, the instructed-assembly to handle nanoarchitectonics of ordered molecular superstructures upon at least one trigger event including receptor-ligand interaction and some reactions.[91] It provides spatiotemporal regulation on transformation from a starting equilibrium to another one, which can be possibly utilized for molecular imaging, tissue engineering, and cancer therapy. The instructed-assembly will be also available for dynamics of molecular processes to control cell fate.

As interfacial nanoarchitectonics to control cell fate, Minami and co-workers reported modulation of cell differentiations of mouse skeletal myoblast C2C12 cells on interfacially nanoarchitected arrays of super-hard materials of fullerene nanowhiskers (Figure 11).[92] Fullerene nanowhiskers are needle-like objects of one-dimensional fullerene assemblies that can be synthesized by the liquid–liquid interfacial precipitation method, be aligned at the air–water interface with appropriate lateral pressures, and be transferred on to a sold surface by the LB technique. The cells grew along with the aligned fullerene

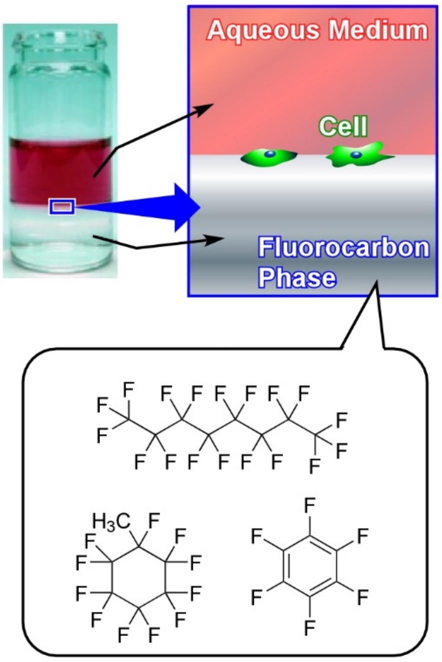

Figure 12 Culture of C2C12 myoblast cells at super-soft liquid interface between fluorocarbon fluid and culture medium.

nanowhiskers with shape shifting. For example, myoblasts expended with elongated morphologies having distinctly high aspect ratios on the aligned nanowhisker arrays, while the cells in a polygonal shape were observed on a bare glass and on the surface of the random nanowhisker arrays. In addition, large fusion index values were observed for the cells grown on the highly aligned arrays of fullerene nanowhiskers. Furthermore, the gene expression level of MyoD in the cells on the aligned fullerene nanowhiskers became 1.35 times higher than that observed for the cells on the surface of bare glasses. The obtained results on up-regulation of the myogenic genes indicated that acceleration of the early and late stages of myogenic differentiation on the aligned fullerene nanowhiskers. The similar cell controls were also investigated on curvature-controlled alignments of fullerene nanowhisker arrays that were fabricated by the vortex LB method with circular liquid flow at the interface.[93] In this case, preferential growth of human osteoblast MG63 cells along with the direction of alignment nanowhiskers was again observed.

In contrast to arrays of super-hard materials, super-soft interfaces, liquid themselves, can be used as cell culture substrates. Rosenberg firstly introduced the use of a fluid substrate for the growth of both transformed and anchorage-dependent cells in 1964.[94] In 1983, Keese and Giaever subsequently demonstrated the use of perfluorocarbon–water interfaces for cell culture, and the use of additives for the formation of thin layers of protein at an interface as a substrate.[95] These pioneering research efforts were then followed by the several examples for the interfacial cell culture at the liquid–liquid interfaces.[96] As epoch-making finding, Minami and co-workers first demonstrated suppression of myogenic differentiation of mammalian cells caused at the liquid–liquid interface in 2017.[97] In 2018, this discovery was expanded to stem cell cultures by Gautrot and co-workers.[98]

Minami and co-workers successfully demonstrated cell adhesion and growth of C2C12 myoblasts at liquid interface between fluorocarbon fluid and culture medium where strains between cell and substrate are expected to be significantly diminished (Figure 12).[97] On the conventional super-hard substrates, C2C12 cells was clearly differentiated in differentiation medium as indicated by significant up-regulation of muscle specific gene expression level (MHC; myosin heavy chain). In contrast, the liquid–liquid interface induced remarkable attenuation of expression of myogenin, a transcription factor in the early stages of differentiation of C2C12. The stiffness of a substrate is important in myogenic differentiation of C2C12 cells. Due to super-soft nature of the liquid–liquid interface, traction forces exerted by cells are significantly weakened, and thereby myogenic differentiation of C2C12 myoblasts is suppressed. In clinical applications, adult stem cells easily lose their stemness accompanied with differentiation on conventional plastic culture dish. The results indicated the potential applications of interfacial culture system for the retention of stemness. Because cell culture at liquid–liquid interface enables us to transfer living cells onto a solid substrate as LB films of living cells, this methodology would open new avenue for the tissue engineering. Architecting living cells into regulated structures can be regarded as an ultimate example of soft materials nanoarchitectonics.

6. Conclusion and perspective

In this review article, various research examples on soft materials nanoarchitectonics are briefly explained especially from viewpoints of sciences and technologies at interfacial environments including interfacial molecular recognition, fabrication of 2D structures and materials, LbL materials constructions, hierarchical structural formation, and cell cultures. Accomplishments of these processes surely and heavily depend on successful designs of unit molecules. In addition, the obtained nanoarchitected materials have wide-ranged possibilities in engineering applications such as environmental sensing and remediation, and biomedical usages including tissue engineering and cell fate regulation. Especially, soft natures of component materials and interfacial environments as working media are crucial keys of these nanoarchitectonics processes from molecular systems design to future engineering applications.

Common features of the exemplified research examples are dynamic natures for advanced functions. Therefore, development of methodologies on precise controls of molecular dynamisms at interfacial media would be the next-generation target in soft materials nanoarchitectonics. Regulations of a single molecule such as molecular machines and nanocars with precise observations and manipulations have become possible by sophisticated nanotechnology with advanced tools, mainly scanning tunnelling microscopy under ultra-high vacuum at lower temperature.[99] Such efforts based

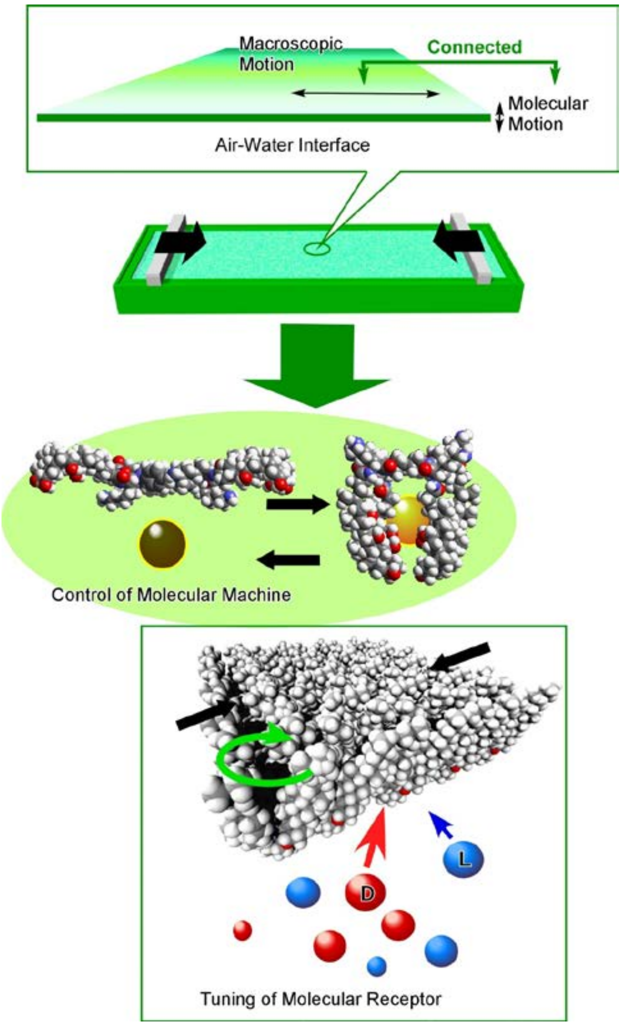

Figure 13 Controls of nanoscopic motions and functions of molecular machines and receptors embedded at the air–water interface by mechanical motions, lateral compression and expansions of a single molecular film (Langmuir monolayer) in tens of centimeters.

on high-level nanotechnology performances would clarify the importance of molecular system designs on dynamic functions. It would be one future direction of the soft materials nanoarchitectonics.

In contrast to the above-mentioned precise molecular controls under ultra-clean conditions, molecular controls under ambient conditions have also great contributions on dynamic functions in realistic materials usages. We have been proposing important roles of the interfacial media to control molecular motions and their functions by ambient and conventional external stimulus such as macroscopic mechanical motions (Figure 13).[100] Because dynamic interfaces such as the air–water interface can couple macroscopic ambient motions along lateral directions and precise molecular functions within nanoscale thickness. Controls of nanoscopic motions and functions of molecular machines and receptors embedded at the air–water interface is possible by mechanical motions, lateral compression and expansions of a single molecular film (Langmuir monolayer) in tens of centimeters.[101] Various examples on regulations of molecular functions including capture and release of a guest molecule,[102] pressure modulated enantioselective recognition of amino acids,[103] precise discrimination between thymine and uracil derivatives,[104] mechanically controlled indicator displacement assay,[105] closure of molecular pliers in both analogue mode[106] and digital mode,[107] and motional regulation of molecular rotors[108] have been accomplished by macroscopic mechanical stimuli.

The nanoarchitectonics concept provides rational strategies to create functional materials with deep relations with molecular system designs that are especially useful for the developments of functions of soft materials. Including essence of interfacial science would also supply important factor of connection of molecular functions and ambient motions. Upon reconsidering important aspects as seen in molecular architectonics,[109] self-assembly-based nanoarchitectonics,[110] two-dimensional interfacial nanoarchitectonics,[111] and bio-related nanoarchitectonics,[112] various applications and engineering outputs in device, materials, energy and bio technology[113] can be continuously created. We expect that molecular system designs can be rationally connected with realistic engineering outputs upon combining the above-mentioned methodologies.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This study was partially supported by JSPS KAKENHI Grant Number JP16H06518 (Coordination Asymmetry) and CREST JST Grant Number JPMJCR1665.

Notes and references

1 A. Vinu, P. Srinivasu, D. P. Sawant, T. Mori, K. Ariga, J.-S. Chang, S.-H. Jhung, V. V. Balasubramanian and Y. K. Hwang, *Chem. Mater.*, 2007, **19**, 4367; K. K. R. Datta, S. B. V. Subba, K. Ariga and A. Vinu, *Angew. Chem. Int. Ed.*, 2010, **49**, 5961; M. Hu, J. Reboul, S. Furukawa, N. L. Torad, Q. Ji, P. Srinivasu, K. Ariga, S. Kitagawa and Y. Yamauchi, *J. Am. Chem. Soc.*, 2012, **134**, 2864; N. Chatani, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 211; S. Zhang, S. Guo, Z. Chen, Y. Wang, H. Gao, J. Gomez-Herrero, P. Ares, F. Zamora, Z. Zhu and H. Zeng, *Chem. Soc. Rev.*, 2018, **47**, 982; I. Saptiama, Y. V. Kaneti, Y. Suzuki, K. Tsuchiya, N. Fukumitsu, T. Sakae, J. Kim, Y.-M. Kang, K. Ariga and Y. Yamauchi, *Small*, 2018, **14**, 1800474.
2 B. Chen, Y. Ding, X. Li, W. Zhu, J. P. Hill, K. Ariga and Y. Xie, *Chem. Commun.*, 2013, **49**, 10136; W. P. Lustig, S. Mukherjee, N. D. Rudd, A. V. Desai, J. Li and S. K. Ghosh, *Chem. Soc. Rev.*, 2017, **46**, 3242; I. Stassen, N. Burtch, A. Talin, P. Falcaro, M. Allendorf and R. Ameloot, *Chem. Soc. Rev.*, 2017, **46**, 3185; Q. Ji, X. Qiao, X. Liu, H. Jia, J. S. Yu and K. Ariga, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 391; J. Sasaki, M. Suzuki and K. Hanabusa, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 538.
3 N. L. Torad, M. Hu, S. Ishihara, H. Sukegawa, A. Belik, M. Imura, K. Ariga, Y. Sakka and Y. Yamauchi, *Small*, 2014, **10**, 2096; F. C. Moreira, R. A. R. Boaventura, E. Brillas and V. J. P. Vilar, *Appl. Catal. D Environ.*, 2017, **202**, 217; X. Liu, J. Iocozzia, Y. Wang, X. Cui, Y. Chen, S. Zhao, Z. Li and Z. Lin, *Energy Environ. Sci.*, 2017,

10, 402; K. Ishimaki, T. Uchiyama, M. Okazaki, D. Lu, Y. Uchimoto and K. Maeda, *Bull. Chem. Soc. Jpn.,* 2018, **91**, 486; S. Yu, X. Wang, H. Pang, R. Zhang, W. Song, D. Fu, T. Hayat and X. Wang, *Chem. Eng. J.*, 2018, **333**, 343.

4 W. Chaikittisilp, H.-S. Huang, M. Hu, T. Fujita, K. C.-W. Wu, L.-C. Chen, Y. Yamauchi and K. Ariga, *Chem. Commun.*, 2012, **48**, 7259; D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo and J. Nakamura, *Science*, 2016, **351**, 361; Y. Yamada, T. Yamada and Y. Kanemitsu, *Bull. Chem. Soc. Jpn.,* 2017, **90**, 1129; S. Stauss and I. Honma, *Bull. Chem. Soc. Jpn.,* 2018, **91**, 492; P. K. Nayak, L. Yang, W. Brehm and P. Adelhelm, *Angew. Chem. Int. Ed.*, 2018, **57**, 102; T. Miyasaka, *Bull. Chem. Soc. Jpn.,* 2018, **91**, 1058; M. Watanabe, K. Dokko, K. Ueno and M. L. Thomas, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 1660; D. R. Dekel, *J. Power Sources*, 2018, **375**, 158.

5 K. Krishnan, M. Muruganathan, T. Tsuruoka, H. Mizuta and M. Aono, *Adv. Funct. Mater.*, 2017, **27**, 1605104; F. Yang, M. Suda and H. M. Yamamoto, *Bull. Chem. Soc. Jpn.,* 2017, **90**, 1259; F. Yao, P. Gui, Q. Zhang and Q. Lin, *Mol. Syst. Des. Eng.*, 2018, **3**, 702; Y. Kobayashi, *Bull. Chem. Soc. Jpn.,* 2018, **91**, 467; A. Yamamura, S. Watanabe, M. Uno, M. Mitani, C. Mitsui, J. Tsurumi, N. Isahaya, Y. Kanaoka, T. Okamoto and J. Takeya, *Sci. Adv.* 2018, **4**, eaao5758.

6 Y. Yoshida and S. Yamanaka, *Circ. Res.*, 2017, **120**, 1958; I. Saptiama, Y. V. Kaneti, Y. Suzuki, Y. Suzuki, K. Tsuchiya, T. Sakae, K. Takai, N. Fukumitsu, Z. A. Alothman, M. S. A. Hossain, K. Ariga and Y. Yamauchi, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 1174; S. Ufaz, A. Balter, C. Tzror, S. Einbender, O. Koshet, J. Shainsky-Roitman, Z. Yaari and A. Schroeder, *Mol. Syst. Des. Eng.*, 2018, **3**, 38; A. Harada and K. Kataoka, *Polym. J.*, 2018, **50**, 95; I. Saptiama, Y. V. Kaneti, H. Oveisi, Y. Suzuki, K. Tsuchiya, K. Takai, T. Sakae, S. Pradhan, M. S. A. Hossain, N. Fukumitsu, K. Ariga and Y. Yamauchi, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 195.

7 C. Tan, X. Cao, X.-J. Wu, Q. He, J. Yang, X. Zhang, J. Chen, W. Zhao, S. Han, G.-H. Nam, M. Sindoro and H. Zhang, *Nat. Rev. Cancer*, 2017, **17**, 20; T. Kitamura and Y. Niidome, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 161; H. Shirai, M. T. Nguyen, D. Cempel, H. Tsukamoto, T. Tokunaga, Y.-C. Liao and T. Yonezawa, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 279; S. Dang, Q.-L. Zhu and Q. Xu, *Nat. Rev. Mater.*, 2018, **3**, 17075; K. Zheng, M. I. Setyawati, D. T. Leong and J. Xie, *Coord. Chem. Rev.*, 2018, **357**, 1.

8 M. Wei, Y. Gao, X. Li and M. J. Serpe, *Polym. Chem.*, 2017, **8**, 127; Y. Wang and T. Michinobu, *Bull. Chem. Soc. Jpn.,* 2017, **90**, 1388; W. Lu, X. Le, J. Zhang, Y. Huang and T. Chen, *Chem. Soc. Rev.*, 2017, **46**, 1284; M. Irie and M. Morimoto, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 237; K. Sada, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 1282; P. Weis and S. Wu, *Macromol. Rapid Commun.*, 2018, **39**, 1700220.

9 G. Povie, Y. Segawa, T. Nishihara, Y. Miyauchi and K. Itami, *Science*, 2017, **356**, 172; J. Yamaguchi and K. Itami, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 367; K. Takimiya and M. Nakano, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 121; Y. Koga, T. Kaneda, Y. Saito, K. Murakami and K. Itami, *Science*, 2018, **359**, 435; S. Hiroto, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 829; Z. Sun, T. Matsuno and H. Isobe, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 907; T. Sugahara, J.-D. Guo, T. Sasamori, S. Nagase and N. Tokitoh, *Angew. Chem. Int. Ed.*, 2018, **57**, 3499.

10 K. Katagiri, M. Hashizume, K. Ariga, T. Terashima and J. Kikuch, *Chem. Eur. J.*, 2007, **13**, 5272; K. Ariga, J. P. Hill, M. V. Lee, A. Vinu, R. Charvet and S. Acharya, *Sci. Technol. Adv. Mater.*, 2008, **9**, 014109; K. Ariga, M. Naito, Q. Ji and D. Payra, *CrystEngComm*, 2016, **18**, 4890; T. Sagami, S. Umemoto, Y. O. Tahara, M. Miyata, Y. Yonamine, D. Ishikawa, T. Mori, K. Ariga, H. Miyake and S. Shinoda, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 739; V. F. Korolovych, A. J. Erwin, A. Stryutsky, E. K. Mikan, V. V. Shevchenko and V. V. Tsukruk, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 919; .S. Cherumukkil, B. Vedhanarayanan, G. Das, V. K. Praveen and A. Ajayaghosh, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 100; T. Shimizu, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 623; S. Dhiman and S. J. George, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 687; S. Hiraoka, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 957.

11 W. Chaikittisilp, K. Ariga and Y. Yamauchi, *J. Mater. Chem. A*, 2013, **1**, 14; V. Malgras, Q. Ji, Y. Kamachi, T. Mori, F.-K. Shieh, K. C.-W. Wu, K. Ariga and Y. Yamauchi, *Bull. Chem. Soc. Jpn.*, 2015, **88**, 1171; L. Yu, H. B. Wu and X. W. D. Lou; *Acc. Chem. Res.*, 2017, **50**, 293; G. Lai and T.-Y. Luh, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 262; L. Wang, X. Jiao, P. Liu, Y. Ouyang, X. Xia, W. Lei and Q. Hao, *Appl. Surf. Sci.*, 2018, **427**, 174.

12 F. Hong, F. Zhang, Y. Liu and H. Yan, *Chem. Rev.*, 2017, **117**, 12584; K. Matsuura *Bull. Chem. Soc. Jpn.*, 2017, **90**, 873; K. V. Presnell and H. S. Alper, *Mol. Syst. Des. Eng.*, 2018, **3**, 13; Y. Goto and H. Suga, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 410; T. Sawada and T. Serizawa, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 455; N. C. Seeman and H. F. Sleiman, *Nat. Rev. Mater.*, 2018, **3**, 17068.

13 L. Syedmoradi, M. Daneshpour, M. Alvandipour, F. A. Gomez, H. Hajghassem and K. Omidfar, *Biosens. Bioelectron.*, 2017, **87**, 373; M. Kiguchi and S. Fujii, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 1; M. Taniguchi, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 1189; R. Chen, J. Kang, M. Kang, H. Lee and H. Lee, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 979; X. Chen and L. Zhang, *Sens. Actuat. B Chem.*, 2018, **254**, 648.

14 K. Ariga, Y. Yamauchi and M. Aono, *APL Mater.*, 2015, **3**, 061001; K. Ariga, Q. Ji, W. Nakanishi, J. P. Hill and M. Aono, *Mater. Horiz.*, 2015, **2**, 406; M. Aono and K. Ariga, *Adv. Mater.*, 2016, **28**, 989.

15 K. Ariga and M. Aono, *Jpn. J. Appl. Phys.*, 2016, **55**, 1102A6.

16 G. Markovich, C. P. Collier, S. E. Henrichs, F. Remacle, R. D. Levine and J. R. Heath, *Acc. Chem. Res.*, 1999, **32**, 415.

17 K. Ariga, Q. Ji, J. P. Hill, Y. Bando and M. Aono, *NPG Asia Mater.*, 2012, **4**, e17.

18 S. Hecht, *Angew. Chem., Int. Ed.*, 2003, **42**, 24.

19 K. Ariga, M. Li, G. J. Richards and J. P. Hill, *J. Nanosci. Nanotechnol.*, 2011, **11**, 1.

20 K. Ariga, A. Vinu, Y. Yamauchi, Q. Ji and J. P. Hill, *Bull. Chem. Soc. Jpn.*, 2012, **85**, 1; W. Nakanishi, K. Minami, L. K. Shrestha, Q. Ji, J. P. Hil and K. Ariga, *Nano Today*, 2014, **9**, 378; M. Osada and T. Sasaki, *Dalton Trans.*, 2018, **47**, 2841; D. Sangian, Y. Ide, Y. Bando, A. E. Rowan and Y. Yamauchi, *Small*, 2018, **14**, 1800551.

21 M. Ramanathan, L. K. Shrestha, T. Mori, Q. Ji, J. P. Hill and K. Ariga, *Phys. Chem. Chem. Phys.*, 2013, **15**, 10580; L. K. Shrestha, K. M. Strzelczyk, R. G. Shrestha, K. Ichikawa, K. Aramaki, J. P. Hill and K. Ariga, *Nanotechnology*, 2015, **26**, 204002; L. Zhang, T. Wang, Z. Shen and M. Liu, *Adv. Mater.*, 2016, **28**, 1044; K. Ariga, V. Malgras, Q. Ji, M. B. Zakaria and Y. Yamauchi, *Coord. Chem. Rev.*, 2016, **320-321**, 139; A. Lorenzo, M. L. Cortez, A. Lorenzo, W. A. Marmisolle, C. von Bilderling, E. Maza, L. Pietrasanta, F. Battaglini, M. Ceolin and O. Azzaroni, *Soft Matter*, 2018, **14**, 1939; W. A. Marmisolle, E. M. Maza, M. Ceolin and O. Azzaroni, *Phys. Chem. Chem. Phys.*, 2018, **20**, 7570.

22 S. Ishihara, J. Labuta, W. Van Rossom, D. Ishikawa, K. Minami, J. P. Hill and K. Ariga, *Phys. Chem. Chem. Phys.*, 2014, **16**, 9713; K. Ariga, K. Minami and L. K. Shrestha, *Analyst*, 2016, **141**, 2629; M. Pandeeswar, S. P. Senanayak and T. Govindaraju, *ACS Appl. Mater. Interfaces*, 2016, **8**, 30362; M. Komiyama, T. Mori and K. Ariga, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 1075; J. A. Jackman, N.-J. Cho, M. Nishikawa, G. Yoshikawa, T. Mori, L. K. Shrestha and K. Ariga, *Chem. Asian J.*, 2018, **13**, 3366.

23 K. Takada, N. Ohta and Y. Tateyama, *J. Inorg. Organomet. Polym. Mater.*, 2015, **25**, 205; Q. Zou, K. Liu, M. Abbas and X. Yan, *Adv. Mater.*, 2016, **28**, 1031; J. Kim, J. H. Kim and K. Ariga, *Joule*, 2017, **1**, 739; .L. K. Shrestha, R. G. Shrestha, S. Joshi, R. Rajbhandari, N. Shrestha, M. P. Adhikari, R. R. Pradhananga and K. Ariga, *J. Inorg. Organomet. Polym. Mater.*, 2017, **27(Suppl 1)**, S48.

24 K. Ariga, S. Ishihara, H. Abe, M. Li and J. P. Hill, *J. Mater. Chem.*, 2012, **22**, 2369; K. Ariga, J. A. Jackman, N.-J. Cho, S.-H. Hsu, L. K. Shrestha, T. Mori and J. Takeya, *Chem. Rec.*, in press. DOI: 10.1002/tcr.201800103.

25 H. Abe, J. Liu and K. Ariga, *Mater. Today*, 2016, **19**, 12; K. Ariga, S. Ishihara and H. Abe, *CrystEngComm*, 2016, **18**, 6770; H. Wang, S. Yin, K. Eid, Y. Li, Y. Xu, X. Li, H. Xue and L. Wang, *ACS Sus. Chem. Eng.*, 2018, **6**, 11768.

26 K. Ariga, S. Watanabe, T. Mori and J. Takeya, *NPG Asia Mater.*, 2018, **10**, 90; A. Nayak, S. Unayama, S. Tai, T. Tsuruoka, R. Waser, M. Aono, I. Valov and T. Hasegawa, *Adv. Mater.* 2018, **30**, 1703261; Y. Yan, J. Ye, K. Wang, J. Yao and Y. S. Zhao, *Small*, 2018, **14**, 1702698.

27 K. Ariga, Q. Ji, M. J. McShane, Y. M. Lvov, A. Vinu and J. P. Hill, *Chem. Mater.*, 2012, **24**, 728; K. Ariga, Q. Ji, T. Mori, M. Naito, Y. Yamauchi, H. Abe and J. P. Hill, *Chem. Soc. Rev.*, 2013, **42**, 6322; K. Ariga, K. Kawakami, M. Ebara, Y. Kotsuchibashi, Q. Ji and J. P. Hill, *New J. Chem.*, 2014, **38**, 5149; E. Stulz, *Acc. Chem. Res.*, 2017, **50**, 823; K. Ariga, D. L. Leong and T. Mori, *Adv. Funct. Mater.*, 2018, **28**, 1702905.

28 K. Ariga, J. Li, J. Fei, Q. Ji and J. P. Hill, *Adv. Mater.*, 2016, **28**, 1251; K. Ariga, *Mater. Chem. Front.*, 2017, **1**, 208.

29 K. Ariga, M. V. Lee, T. Mori, X.-Y. Yu and J. P. Hill, *Adv. Colloid Interface Sci.*, 2010, **154**, 20; K. Ariga, T. Mori and J. P. Hill, *Langmuir*, 2013, 29, 8459; K. Ariga, Q. Ji, W. Nakanishi and J. P. Hill, *J. Inorg. Organomet. Polym. Mater.*, 2015, **25**, 466.

30 K. Ariga, T. Mori and J. Li, *Langmuir*, in press. DOI: 10.1021/acs.langmuir.8b01434

31 K. Ariga, H. Ito, J. P. Hill and H. Tsukube, *Chem. Soc. Rev.*, 2012, **41**, 5800.

32 K. Ariga and T. Kunitake, *Acc. Chem. Res.*, 1998, **31**, 371; K. Ariga, *ChemNanoMat*, 2016, **2**, 333.

33 B. Springs and P. Haake, *Bioorg. Chem.*, 1977, **6**, 181.

34 M. Onda, K. Yoshihara, H. Koyano, K. Ariga and T. Kunitake, *J. Am. Chem. Soc.*, 1996, **118**, 8524.

35 D. Y. Sasaki, K. Kurihara and T. Kunitake, *J. Am. Chem. Soc.*, 1991, **113**, 9685; D. Y. Sasaki, K. Kurihara and T. Kunitake, *J. Am. Chem. Soc.*, 1992, **114**, 10994.

36 M. Sakurai, H. Tamagawa, Y. Inoue, K. Ariga and T. Kunitake, *J. Phys. Chem. B*, 1997, **101**, 4810; H. Tamagawa, M. Sakurai, Y. Inoue, K. Ariga, and T. Kunitake, *J. Phys. Chem. B*, 1997, **101**, 4817.

37 K. Kurihara, K. Ohto, Y. Tanaka, Y. Aoyama and T. Kunitake, *J. Am. Chem. Soc.*, 1991, **113**, 444; K. Ariga, K. Isoyama, O. Hayashida, Y. Aoyama and Y. Okahata, *Chem. Lett.* 1998, 1007.

38 Y. Ikeura, Y. Honda, K. Kurihara and T. Kunitake, *Chem. Lett.*, 1990, 169: Y. Ikeura, K. Kurihara and T. Kunitake, *J. Am. Chem. Soc.*, 1991, **113**, 7342.

39 K. Taguchi, K. Ariga and T. Kunitake, *Chem. Lett.*, 1995, 701; K. Ariga, A. Kamino, H. Koyano and T. Kunitake, *J. Mater. Chem.*, 1997, **7**, 1155.

40 T. Kawahara, K. Kurihara and T. Kunitake, *Chem. Lett.*, 1992, 1839.

41 X. Cha, K. Ariga, M. Onda and T. Kunitake, *J. Am. Chem. Soc.*, 1995, **117**, 11833; X. Cha, K. Ariga and T. Kunitake, *J. Am. Chem. Soc.*, 1996, **118**, 9545; K. Ariga, A. Kamino, X. Cha and T. Kunitake, *Langmuir*, 1999, **15**, 3875.

42 K. Ariga, *J. Nanosci. Nanotechnol.*, 2004, **4**, 23; K. Sakakibara, J. P. Hill and K. Ariga, *Small*, 2011, **7**, 1288.

43 Y. Oishi, T. Kato, M. Kuramori, K. Suehiro, K. Ariga, A. Kamino, H. Koyano and T. Kunitake, *Chem. Commun.*, 1997, 1357.

44 H. Koyano, K. Yoshihara, K. Ariga, T. Kunitake, Y. Oishi, O. Kawano, M. Kuramori and K. Suehiro, *Chem. Commun.*, 1996, 1769.

45 Y. Oishi, Y. Torii, M. Kuramori, K. Suehiro, K. Ariga, K. Taguchi, A. Kamino and T. Kunitake, *Chem. Lett.*, 1996, 411; Y. Oishi, Y. Torii, T. Kato, M. Kuramori, K. Suehiro, K. Ariga, K. Taguchi, A. Kamino, H. Koyano and T.Kunitake, *Langmuir*, 1997, **13**, 519.

46 M. Mukai and S. L. Regen, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 1083.

47 X. Liu, J. G. Riess and M. P. Krafft, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 846.

48 Y. Oishi, T. Kato, T. Narita, K. Ariga and T. Kunitake, *Langmuir*, 2008, **24**, 1682.

49 T. Seki, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 1026.

50 K. Sakakibara, P. Chithra, B. Das, T. Mori, M. Akada, J. Labuta, T. Tsuruoka, S. Maji, S. Furumi, L. K. Shrestha, J. P. Hill, S. Acharya, K. Ariga and A. Ajayaghosh, *J. Am. Chem. Soc.*, 2014, **136**, 8548.

51 R. Sakamoto, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 272.

52 H. Koyano, P. Bissel, K. Yoshihara, K. Ariga and T. Kunitake, *Langmuir*, 1997, **13**, 5426; H. Koyano, P. Bissel, K. Yoshihara, K. Ariga and T. Kunitake, *Chem. Eur. J.*, 1997, **3**, 1077.

53 Y. Yonamine, K. Cervantes-Salguero, K. Minami, I. Kawamata, W. Nakanishi, J. P. Hill, S. Murata and K. Ariga, *Phys. Chem. Chem. Phys.*, 2016, **18**, 12576.

54 Y. Yonamine, K. Cervantes-Salguero, W. Nakanishi, I. Kawamata, K. Minami, H. Komatsu, S. Murata, J. P. Hill and K. Ariga, *Phys. Chem. Chem. Phys.*, 2015, **17**, 32122.

55 T. Mori, H. Tanaka, A. Dalui, N. Mitoma, K. Suzuki, M. Matsumoto, N. Aggarwal, A. Patnaik, S. Acharya, L. K. Shrestha, H. Sakamoto, K. Itami and K. Ariga, *Angew. Chem. Int. Ed.*, 2018, **57**, 9679.

56 T. Low, A. Chaves, J. D. Caldwell, A. Kumar, N. X. Fang, P. Avouris, T. F. Heinz, F. Guinea, L. Martin-Moreno and F. Koppens, *Nat. Mater.*, 2017, **16**, 182; K. Takase, H. Nishizawa, K. Imamura, A. Onda, K. Yanagisawa and S. Yin, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 1546; M. Matsumoto, Y. Mizutani and M. Aoki, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 1205.

57 V. C. Rodrigues, M. L. Moraes, J. C. Soares, A. C. Soares, R. Sanfelice, E. Deffune and O. N. Oliveira, Jr., *Bull. Chem. Soc. Jpn.*, 2018, **91**, 891.

58 E. Ruiz-Hitzky, A. Gómez-Avilés, M. Darder and P. Aranda, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 608.

59 S. Acharya, J. P. Hill and K. Ariga, *Adv. Mater.*, 2009, **21**, 2959; K. Ariga, Y. Yamauchi, T. Mori and J. P. Hill, *Adv. Mater.*, 2013, **25**, 6477.

60 K. Ariga, Y. M. Lvov, K. Kawakami, Q. Ji and J. P. Hill, *Adv. Drug Deliv. Rev.*, 2011, **63**, 762; K. Ariga, Y. Yamauchi, G. Rydzek, Q. Ji, Y. Yonamine, K. C.-W. Wu and J. P. Hill, *Chem. Lett.*, 2014, **43**, 36; G. Rydzek, Q. Ji, M. Li, P. Schaaf, J. P. Hill, F. Boulmedais and K. Ariga, *Nano Today*, 2015, **10**, 138.

61 G. Decher, *Science*, 1997, **277**, 1232.

62 W. B. Stockton and M. F. Rubner, *Macromolecules*, 1997, **30**, 2717; L. Wang, Z. Wang, X. Zhang, J. Shen, L. Chi and H. Fuchs, *Macromol. Rapid Commun.*, 1997, **18**, 509.

63 H. Lee, L. J. Kepley, H.-G. Hong and T. E. Mallouk, *J. Am. Chem. Soc.*, 1988, **110**, 618; S. W. Keller, H.-N. Kim and T. E. Mallouk, *J. Am. Chem. Soc.*, 1994, **116**, 8817.

64 A. Ikeda, T. Hatano, S. Shinkai, T. Akiyama and S. Yamada, *J. Am. Chem. Soc.*, 2001, **123**, 4855.

65 W. Muller, H. Ringsdorf, E. Rump, G. Wildburg, X. Zhang, L. Angermaier, W. Knoll, M. Liley and J. Spinke, *Science*, 1993, **262**, 1706; Y. Lvov, K. Ariga, I. Ichinose and T. Kunitake, *J. Chem. Soc., Chem. Commun.*, 1995, 2313.

66 Y. Shimazaki, M. Mitsuishi, S. Ito and M. Yamamoto, *Langmuir*, 1997, **13**, 1385.

67 T. Serizawa, K.-i. Hamada, T. Kitayama, N. Fujimoto, K. Hatada and M. Akashi, *J. Am. Chem. Soc.*, 2000, **122**, 1891; T. Serizawa, K. Hamada and M. Akashi, *Nature*, 2004, **429**, 52.

68 J. Cho, K. Char, J.-D. Hong and K.-B. Lee, *Adv. Mater.*, 2001, **13**, 1076; S.-S. Lee, J.-D. Hong, C. H. Kim, K. Kim, J. P. Koo and K.-B. Lee, *Macromolecules*, 2001, **34**, 5358.

69 S. L. Clark and P. T. Hammond, *Adv. Mater.*, 1998, **10**, 1515; S. S. Shiratori and M. Yamada, *Polym. Adv. Technol.*, 2000, **11**, 810.

70 M. Lefort, G. Popa, E. Seyrek, R. Szamocki, O. Felix, J. Hemmerlé, L. Vidal, J.-C. Voegel, F. Boulmedais, G. Decher and P. Schaaf, *Angew. Chem., Int. Ed.*, 2010, **49**, 10110.

71 G. B. Sukhorukov, E. Donath, S. Davis, H. Lichtenfeld, F. Caruso, V. I. Popov and H. Möhwald, *Polym. Adv. Technol.*, 1998, **9**, 759; E. Donath, G. B. Sukhorukov, F. Caruso, S. A. Davis and H. Möhwald, *Angew. Chem. Int. Ed.*, 1998, **37**, 2201; F. Caruso, R. A. Caruso and H. Möhwald, *Science*, 1998, **282**, 1111; G. B. Sukhorukov, M. Brumen, E. Donath and H. Möhwald, *J. Phys. Chem. B*, 1999, **103**, 6434.

72 B. Anasori, M. R. Lukatskaya and Y. Gogotsi, *Nat. Rev. Mater.*, 2017, **2**, 16098; A. H. Khan, S. Ghosh, B. Pradhan, A. Dalui, L. K. Shrestha, S. Acharya and K. Ariga, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 627; Y. Wang, C. C. Mayorga-Martinez and M. Pumera, *Bull. Chem.*

Soc. Jpn., 2017, **90**, 847; C. Sengottaiyan, R. Jayavel, P. Bairi and R. G. Shrestha, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 955; S. Zhong and Q. Xu, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 1606.

73 Q. Ji, I. Honma, S.-M. Paek, M. Akada, J. P. Hill, A. Vinu and K. Ariga, *Angew. Chem. Int. Ed.*, 2010, **49**, 9737.

74 K. Ariga, A. Vinu, Q. Ji, O. Ohmori, J. P. Hill, S. Acharya, J. Koike and S. Shiratori, *Angew. Chem. Int. Ed.*, 2008, 47, 7254.

75 Q. Ji, S. B. Yoon, J. P. Hill, A. Vinu, J.-S. Yu and K. Ariga, *J. Am. Chem. Soc.*, 2009, **131**, 4220.

76 Q. Ji, M. Miyahara, J. P. Hill, S. Acharya, A. Vinu, S. B. Yoon, J.-S. Yu, K. Sakamoto and K. Ariga, *J. Am. Chem. Soc.*, 2008, **130**, 2376; Q. Ji, S. Acharya, J. P. Hill, A. Vinu, S. B. Yoon, J.-S. Yu, K. Sakamoto and K. Ariga, *Adv. Funct. Mater.*, 2009, **19**, 1792.

77 B. L. Li, M. I. Setyawati, L. Chen, J. Xie, K. Ariga, C.-T. Lim, S. Garaj and D. T. Leong, *ACS Appl. Mater. Interfaces*, 2017, **9**, 15286.

78 N. Mihara, Y. Yamada and K. Tanaka, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 427.

79 Y. Haketa and H. Maeda, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 420.

80 M. Akamatsu, H. Komatsu, A. Matsuda, T. Mori, W. Nakanishi, H. Sakai, J. P. Hill and K. Ariga, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 678.

81 L. K. Shrestha, M. Sathish, J. P. Hill, K. Miyazawa, T. Tsuruoka, N. M. Sanchez-Ballester, I. Honma, Q. Ji and K. Ariga, *J. Mater. Chem. C*, 2013, **1**, 1174.

82 M. Sathish, K. Miyazawa, J. P. Hill and K. Ariga, *J. Am. Chem. Soc.*, 2009, **131**, 6372; L. K. Shrestha, R. G. Shrestha, J. P. Hill, T. Tsuruoka, Q. Ji, T. Nishimura and K. Ariga, *Langmuir*, 2016, **21**, 12511.

83 K. Miyazawa, *Sci. Technol. Adv. Mater.*, 2015, **16**, 013502.

84 L. K. Shrestha, Y. Yamauchi, J. P. Hill, K. Miyazawa and K. Ariga, *J. Am. Chem. Soc.*, 2013, **135**, 586.

85 L. K. Shrestha, Q. Ji, T. Mori, K. Miyazawa, Y. Yamauchi, J. P. Hill and K. Ariga, *Chem. Asian J.*, 2013, **8**, 1662.

86 P. Bairi, K. Minami, W. Nakanishi, J. P. Hill, K. Ariga and L. K. Shrestha, *ACS Nano*, 2016, **10**, 6631.

87 P. Bairi, K. Minami, J. P. Hill, K. Ariga and L. K. Shrestha, *ACS Nano*, 2017, **11**, 7790.

88 P. Bairi, K. Minami, J. P. Hill, W. Nakanishi, L. K. Shrestha, C. Liu, K. Harano, E. Nakamura and K. Ariga, *ACS Nano*, 2016, **10**, 8796; K. Ariga, T. Mori and L. K. Shrestha, *Chem. Rec.*, 2018, **18**, 676.

89 E. Ruiz-Hitzky, M. Darder, P. Aranda and K. Ariga, *Adv. Mater.*, 2010, **22**, 323; A. Vinu, M. Miyahara and K. Ariga, *J. Nanosci. Nanotechnol.*, 2006, **6**, 1510; M. Komiyama, K. Yoshimoto, M. Sisido and K. Ariga, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 967; J. Sun, D. Zhang, W. Zhao, Q. Ji and K. Ariga, *Bull. Chem. Soc. Jpn.*, in press. DOI: 10.1246/bcsj.20180201

90 C. Igarashi, A. Murata, Y. Itoh, D. R. G. Subekti, S. Takahashi and K. Kamagata, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 34.

91 H. He and B. Xu, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 900.

92 K. Minami, Y. Kasuya, T. Yamazaki, Q. Ji, W. Nakanishi, J. P. Hill, H. Sakai and K. Ariga, *Adv. Mater.*, 2015, **27**, 4020.

93 V. Krishnan, Y. Kasuya, Q. Ji, M. Sathish, L. K. Shrestha, S. Ishihara, K. Minami, H. Morita, T. Yamazaki, N. Hanagata, K. Miyazawa, S. Acharya, W. Nakanishi, J. P. Hill and K. Ariga, *ACS Appl. Mater. Interfaces*, 2015, **7**, 15667.

94 M. D. Rosenberg, Cellular control mechanisms and cancer; Emmelot, P., Mohbock, O., Eds.; Elsevier: Amsterdam, Netherlands, 1964; pp 146-164.

95 I. Giaever and C. R. Keese, *Proc. Natl. Acad. Sci. U. S. A.*, 1983, **80**, 219; C. R. Keese and I. Giaever, *Proc. Natl. Acad. Sci. U. S. A.*, 1983, **80**, 5622; C. R. Keese and I. Giaever, *Exp. Cell Res.*, 1991, **195**, 528.

96 Y. Shiba, T. Ohshima and M. Sato, *Kagaku Kogaku Ronbunshu*, 1998, **24**, 343; Y. Shiba, T. Ohshima and M. Sato, *Biotechnol. Bioeng.*, 1998, **57**, 583; M. Sato, T. Shinozawa, H. Ueno and M. Sadakata, *Kagaku Kogaku Ronbunshu*, 1991, **17**, 671; J. Ando, S. M. Albelda and E. M. Levine, *Dev. Biol.*, 1991, **7A**, 525; M. Pilarek, I. Grabowska, M. A. Ciemerych, K. Dabkowska and K. W. Szewczyk, *Biotechnol. Lett.*, 2013, **35**, 1387.

97 K. Minami, T. Mori, W. Nakanishi, N. Shigi, J. Nakanishi, J. P. Hill, M. Komiyama and K. Ariga, *ACS Appl. Mater. Interfaces*, 2017, **9**, 30553.

98 D. Kong, W. Megone, K. D. Q. Nguyen, S. di Cio, M. Ramstedt and J. E. Gautrot, *Nano Lett.*, 2018, **18**, 1946; D. Kong, L. Peng, S. Di Cio, P. Novak and J. E. Gautrot, *ACS Nano*, 2018, **12**, 9206.

99 Y. Shirai, K. Minami, W. Nakanishi, Y. Yonamine, C. Joachim and K. Ariga, *Jpn. J. Appl. Phys.*, 2016, **55**, 1102A2; W.-H. Soe, Y. Shirai, C. Durand, Y. Yonamine, K. Minami, X. Bouju, M. Kolmer, K. Ariga, C. Joachim and W. Nakanishi, *ACS Nano*, 2017, **11**, 10357; K. Ariga, T. Mori and W. Nakanishi, *Chem. Asian J.*, 2018, **13**, 1266.

100 K. Ariga, T. Mori and J. P. Hill, *Adv. Mater.*, 2012, **24**, 158; K. Ariga, *Anal. Sci.*, 2016, **32**, 1141; K. Ariga, T. Mori, W. Nakanishi and J. P. Hill, *Phys. Chem. Chem. Phys.*, 2017, **19**, 23658; L. K. Shrestha, T. Mori and K. Ariga, *Curr. Opin. Colloid Interface Sci.*, 2018, **35**, 68.

101 K. Ariga, T. Mori, S. Ishihara, K. Kawakami and J. P. Hill, *Chem. Mater.*, 2014, **26**, 519; K. Ariga, K. Minami, M. Ebara and J. Nakanishi, *Polym. J.*, 2016, **48**, 371.

102 K. Ariga, Y. Terasaka, D. Sakai, H. Tsuji and J. Kikuchi, *J. Am. Chem. Soc.*, 2000, **122**, 7835; K. Ariga, T. Nakanishi, Y. Terasaka, H. Tsuji, D. Sakai and J. Kikuchi, *Langmuir*, 2005, **21**, 976.

103 T. Michinobu, S. Shinoda, T. Nakanishi, J. P. Hill, K. Fujii, T. N. Player, H. Tsukube and K. Ariga, *J. Am. Chem. Soc.*, 2006, **128**, 14478; T. Michinobu, S. Shinoda, T. Nakanishi, J. P. Hill, K. Fujii, T. N. Player, H. Tsukube and K. Ariga, *Phys. Chem. Chem. Phys.*, 2011, **13**, 4895.

104 T. Mori, K. Okamoto, H. Endo, J. P. Hill, S. Shinoda, M. Matsukura, H. Tsukube, Y. Suzuki, Y. Kanekiyo and K. Ariga, *J. Am. Chem. Soc.*, 2010, **132**, 12868; T. Mori, K. Okamoto, H. Endo, K. Sakakibara, J. P. Hill, S. Shinoda, M. Matsukura, H. Tsukube, Y. Suzuki, Y. Kanekiyo and K. Ariga, *Nanoscale Res. Lett.*, 2011, **6**, 304.

105 K. Sakakibara, L. A. Joyce, T. Mori, T. Fujisawa, S. H. Shabbir, J. P. Hill, E. V. Anslyn and K. Ariga, *Angew. Chem. Int. Ed.*, 2012, **51**, 9643.

106 D. Ishikawa, T. Mori, Y. Yonamine, W. Nakanishi, D. Cheung, J. P. Hill and K. Ariga, *Angew. Chem. Int. Ed.*, 2015, **54**, 8988.

107 T. Mori, D. Ishikawa, Y. Yonamine, Y. Fujii, J. P. Hill, I. Ichinose, K. Ariga and W. Nakanishi, *ChemPhysChem,*, 2017, **18**, 1470.

108 T. Mori, H. Komatsu, N. Sakamoto, K. Suzuki, J. P. Hill, M. Matsumoto, H. Sakai, K. Ariga and W. Nakanishi, *Phys. Chem. Chem. Phys.*, 2018, **20**, 3073.

109 M. B. Avinash and T. Govindaraju, *Acc. Chem. Res.* 2018, **51**, 414.

110 K. Ariga, M. Nishikawa, T. Mori, J. Takeya, L. K. Shrestha and J. P. Hill, *Sci. Technol. Adv. Mater.*, in press. DOI: 10.1080/14686996.2018.1553108.

111 T. Govindaraju and M. B. Avinash, *Nanoscale*, 2012, **4**, 610.

112 M. B. Avinash and T. Govindaraju, *Nanoscale*, 2014, **6**, 13348; M. Pandeeswar, S. P. Senanayak and T. Govindaraju, *ACS Appl. Mater. Interfaces* 2016, **8**, 30362.

113 K. Tahara, T. Kadowaki, J. Kikuchi, Y. Ozawa, S. Yoshimoto and M. Abe, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 1630; H. Asanuma, K. Murayama, Y. Kamiya and H. Kashida, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 1739; Y. Einaga, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 1752; T. Yonezawa, D. Čempel and M. T. Nguyen, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 1781; F. Peng, M. I. Setyawati, J. K. Tee, X. Ding, J. Wang, M. E. Nga, H. K. Ho and D. T. Leong. *Nat. Nanotechnol.*, in press. DOI: 10.1038/s41565-018-0356-z.

Nanoarchitectonics would be a breakthrough paradigm for preparation of functional materials with soft material components from nanoscale units.