Nanoarchitectonics: Method for Everything in Material Science

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Abstract

Nanotechnology has revealed the science of the nanoscale. The global challenge that will follow is to build up functional materials with the knowledge of nanoscale phenomena. This task is carried out by nanoarchitectonics as a post-nanotechnology concept. The goal of nanoarchitectonics is to build functional material systems by architecting atoms, molecules, and nanomaterials as building blocks. Fundamentally, all materials are made of atoms and molecules. Therefore, nanoarchitectonics, which architects materials from atoms and molecules, can be a universal way to create all materials. It may be said to be the method for everything in material science. From atoms and molecules, which are basic units, to living cells, which are complex systems, are all components of nanoarchitectonics. This paper presents recent examples of nanoarchitectonics research at various size levels, from the atomic to the cellular level, specifically, (i) atomistic nanoarchitectonics, (ii) molecular nanoarchitectonics, (iii) supramolecular nanoarchitectonics, (iv) inorganic nanoarchitectonics, (v) biomolecular nanoarchitectonics, (vi) cell-mimic nanoarchitectonics, and (vii) cell-based nanoarchitectonics. The possibility of nanoarchitectonics, method for everything in materials science, as an integrative challenge will then be explored.

Keywords: Nanoarchitectonics, Method for everything, Materials science

1. Introduction

The exploration and development of new materials is an ongoing global challenge for humankind. The development of human society is deeply dependent on the evolution of material civilization. The quality of life depends on useful materials and the powerful tools produced from them. Humans began by extracting materials from nature, processing them, and using them. In the 20th century, various disciplines of material science developed rapidly and enabled the rational development of functional materials. Organic chemistry,[1] inorganic chemistry,[2] supramolecular chemistry,[3] coordination chemistry,[4] polymer chemistry,[5] other material sciences,[6] and bio-related sciences[7] have all made significant contributions and continue to meet diverse demands in energy,[8] environment,[9] biomedical,[10] and other fields.[11]

These developments in science have shown that matter can be rationally created from atoms and molecules. However, the situation is not simple. It has become clear that the nanoscale structures and effects of the same material can significantly change the material functions. In other words, to obtain higher functions, it is necessary not only to synthesize materials but also to control their internal structures. This requires a better understanding of phenomena in the atomic, molecular, and nanoscale regions. This became the new global challenge. Nanotechnology, which has developed rapidly since the latter half of the 20th century, has been a powerful driving force behind this trend. High-resolution microscopes and measurement techniques allow us to observe atoms and molecules directly.[12] We can examine and manipulate the detailed properties of nanoscale phenomena.[13]
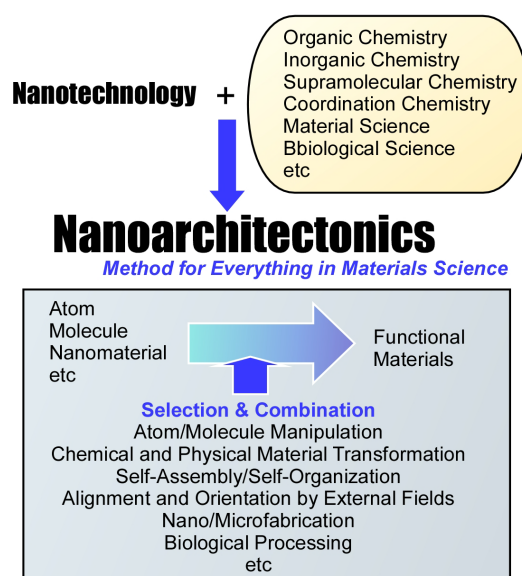

Figure 1. Out line of nanoarchitectonics concept

Nanotechnology has revealed the science of the nanoscale. The global challenge that will follow is to build up functional materials with the knowledge of nanoscale phenomena. This task will be carried out by nanoarchitectonics (Figure 1) as a post-nanotechnology concept.[14] Rather than being an entirely new
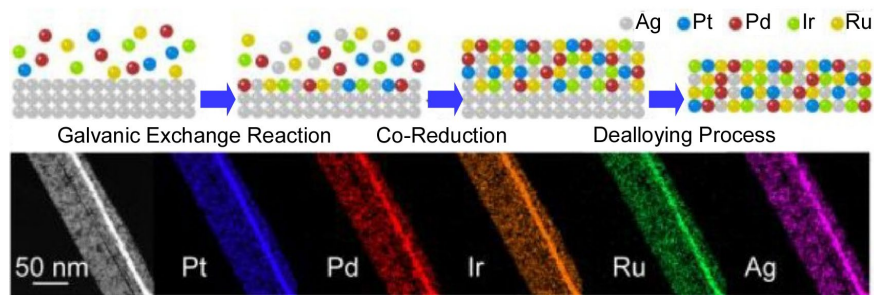
Figure 2. Subnanometer ribbons of ultra-thin high-entropy alloys (PtPdIrRuAg): preparation method and elemental mapping. Reproduced with permission.[38] Copyright 2022, American Chemical Society.

research field, nanoarchitectonics can be thought of as the integration of existing research fields. The goal of nanoarchitectonics is to build functional material systems by architecting atoms, molecules, and nanomaterials as building blocks.[15] It integrates nanotechnology, organic chemistry, inorganic chemistry, polymer chemistry, supramolecular chemistry, coordination chemistry, and material science, as well as microfabrication technology and biological sciences.[16]

The process of building functional molecules from nano is based on atom/molecule manipulation, chemical and physical material transformation, self-assembly/self-organization, alignment and orientation by external fields, nano/microfabrication, and biological processing, which are selected and combination of these processes.[17] Therefore, it is often a multi-step process and tends to form asymmetric and hierarchical structures.[18] Compared to self-assembly based on simple equilibrium processes, this process has the potential for a variety of structural architectures. In addition, the underlying nano-level interactions involve uncertainties such as thermal fluctuations, stochastic distributions, and quantum effects. Therefore, rather than building up the interactions, the entire effects are harmonized.[19] The formation of hierarchical structures and their coexistence with uncertainties such as thermal fluctuations share characteristics with the high level of structural organization in living organisms.[20]

As described above, the methodology of nanoarchitectonics is general and not bound to specific materials or purposes. Therefore, it has a wide range of applications, as exemplified by the wide variety of subjects selected in the papers with nanoarchitectonics in the title. For example, the more basic sciences include the creation of functional materials,[21] structural control,[22] exploration of physical phenomena,[23] and basic biochemical research.[24] Application-oriented research fields used for sensors,[25] devices,[26] catalysts,[27] energy,[28] environmental,[29] and biomedical[30] applications are also included. It can contribute to many areas of functional materials science. Fundamentally, all materials are made of atoms and molecules. Therefore, nanoarchitectonics, which architects matter from atoms and molecules, can be a universal way to create all matter. It may be said to be the method for everything in material science,[31] equivalent to the theory of everything in physics.[32] The methodology to create all matter can be regarded as a big global challenge in material science.

Of course, it is unlikely that method for everything will be achieved instantly. The organization of functional structures in living organisms, with similar processes, has been won over by billions of years of evolution. However, nanoarchitectonics-like studies have already been conducted on parts of it. Therefore, this paper presents recent examples of nanoarchitectonics

research at various size levels, from the atomic to the cellular level, specifically, (i) atomistic nanoarchitectonics, (ii) molecular nanoarchitectonics, (iii) supramolecular nanoarchitectonics, (iv) inorganic nanoarchitectonics, (v) biomolecular nanoarchitectonics, (vi) cell-mimic nanoarchitectonics, and (vii) cell-based nanoarchitectonics. The possibility of nanoarchitectonics, method for everything in materials science, as a global challenge will then be explored.

2. Atomistic Nanoarchitectonics

At the smallest level of nanoarchitectonics, there are examples of functional structures created by collecting atoms. For example, a switch function can be produced by aggregating atoms in a very narrow metal gap.[33] The behavior of this atom switch depends on the potential stimulation frequency of filament formation by atom precipitation. This simple nanoarchitectonics of atoms can lead to synapse-like functions such as short-term plasticity and long-term potentiation.[34] New materials are also created through nanoarchitectonics by designing and gathering atoms in precise numbers and types. Materials with anisotropic and quantum effects are also synthesized by collecting atoms in specific nanospaces. For example, Yamamoto et al. reported the nanoarchitectonics of clusters of a specific number and type of atoms using the controlled space of dendrimers.[35] There are many possibilities for atomistic nanoarchitectonics. It is difficult to focus on specific ones. Here, a limited number of possibilities with a few examples are only described.

High-entropy alloys have attracted attention as a product of nanoarchitectonics,[36] in which atoms are mixed together. In particular, alloys in which five or more elements are mixed in near equal concentrations are often called high-entropy alloys.[37] In high-entropy alloys, the composition can be freely changed, and properties such as specific catalytic properties emerge accordingly. Control of the structure is necessary to realize diverse applications. It is desirable to precisely nanoarchitectonize high-entropy alloys into ultra-thin film low-dimensional nanostructures. However, this is not always easy due to the intrinsic thermodynamic instability of high-entropy alloys. Huang, Guo, and co-workers reported a method for creating subnanometer ribbons of ultra-thin high-entropy alloys (Figure 2).[38] In addition to the example in Figure 2 (PtPdIrRuAg high-entropy alloy), they successfully fabricated quaternary (PtPdIrRuAg), quintet (PtPdIrRuAuAg), quaternary (PtPdIrRuAuRhAg), and octet (PtPdIrRuAuRhOsAg) sub-nanometer ribbons using Ag nanowires as templates with different metal precursors. Galvanic exchange reactions with different metal precursors induced nucleation of different metal atoms. Co-reduction of different metal precursors on this
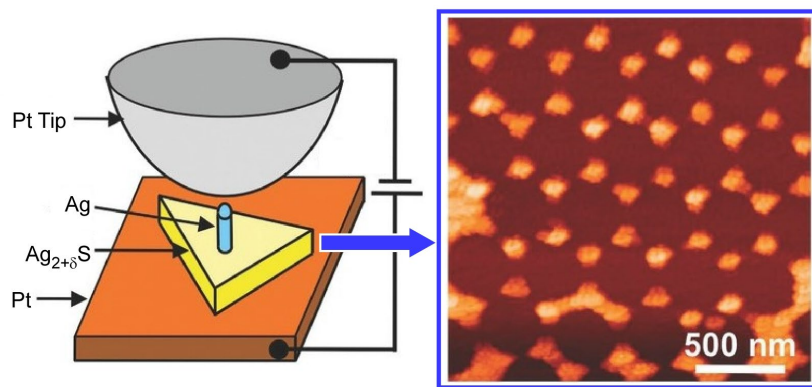
Figure 3. An approach to manipulate the number of dopants in a solid electrolyte on an atomic scale using α-Ag$_{2+\delta}$S nanodots containing non-stoichiometric excess Ag (Ag$^+$ ions and electrons) as a model system. Reproduced with permission.[40] Copyright 2018, Wiley-VCH.

template was carried out. Subnanometer ribbons of ultra-thin high-entropy alloys were then prepared by removal of the Ag core. This synthesis method allows for flexible tuning of the composition and concentration in the high-entropy alloy sub-nanometer ribbons and the construction of a library. As a result, it becomes possible to explore materials with even better electrocatalytic properties. Density functional theory (DFT) calculations have revealed the role of each element and the conditions for higher electroactivity of high-entropy alloy sub-nanometer ribbons. For example, the concentration of highly dynamic reducing elements (Pd, Pt, Ag, Au) is important for electrical activity. On the other hand, relatively inert oxidizing elements (Ir, Ru, Rh, Os) promote efficient electron transfer between sites but can cause localized aggregation. High-entropy alloy subnanometer ribbons nanoarchitectonized from the atomic level were found to perform well as oxygen reduction reaction catalysts in fuel cells, showing high discharge capacity, low charge overpotential, and excellent durability for Li-O$_2$ batteries. One methodology to create optimal functional materials by assembling elements from the atomic level was demonstrated.

As a preparation of multi-element nanoarchitectonics quantum dots, Acharya and coworkers reported the synthesis of colloids of quaternary alloyed CuCdSSe quantum dots.[39] These quantum dots exhibit bright and stable photoluminescence with an absolute luminescence quantum yield of 62%. They fabricated optical waveguide slabs by impregnating these quantum dots with polydimethylsiloxane. The results show that the waveguide slab can collect diffuse light and transmit it over a certain distance. The atomic nanoarchitectonics approach to achieve this large Stokes shift can be generalized to various elemental combinations. It is useful for fabricating high quality transparent and flexible waveguides. Such Stokes shift engineering of quantum dots is an attractive approach for creating materials with high luminescence efficiency by reducing reabsorption losses.
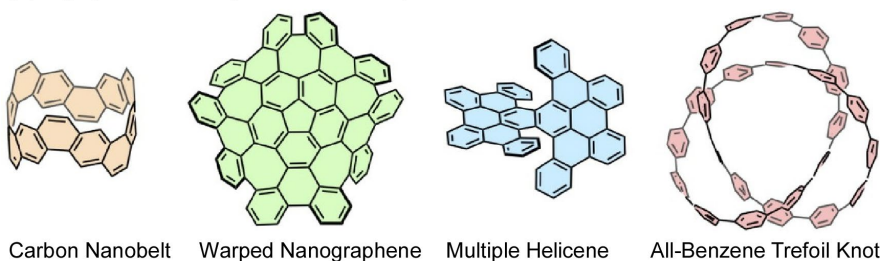
Atomistic nanoarchitectonics for discrete tuning of the electrical properties of materials has also been reported. By restricting the number of dopants to a finite and small value, discrete changes in the electrical properties of a material can be observed Hasegawa and co-workers reported an experimental and theoretical approach to manipulate the number of dopants in a solid electrolyte on an atomic scale (Figure 3).[40] In their atom-nanoarchitectonics approach, the number of dopants can be limited by pre-tuning the size of the target solid electrolyte.

Specifically, this attempt was demonstrated using α-Ag$_{2+\delta}$S nanodots containing non-stoichiometric excess Ag (Ag$^+$ ions and electrons) as a model system. The size of the Ag$_{2+\delta}$S nanodots used was small enough to allow discrete atom-by-atom deposition. Controlled discrete manipulation of dopants was demonstrated by varying the electrochemical potential using scanning tuneling microscope (STM). A limited number of non-stoichiometric dopants allowed atomic deposition by widening the separation between adjacent levels of the electrochemical potential. When the number of movable dopants was small (< 150), the chemical potential was found to be a discrete function of the number of atoms/ions and to vary in a stepwise manner. It was also found that the separation between the atom/ion energy levels and the cohesive energy contribution determines the behavior of the system. This approach will usher in a nanoarchitectonics approach for nanodevice development that relies on single ion/atom transfer.

There have been attempts to create new functions by nanoarchitectonics of anions. Maeda, Kageyama, and co-workers summarize the development of new functional materials consisting of mixed anionic compounds in a recent review article.[41] The functional targets are envisioned to include photoelectrodes, photocatalysts, secondary battery components, thermoelectric conversion materials, phosphors, and conductors. The concept of mixed anionic nanoarchitectonics will lead to material designs that differ from previous design guidelines. For example, in the study of energy-conversion photocatalysts, materials that were not previously considered as candidates due to technical problems or preconceptions have been found to exhibit excellent functions. Anion-doped titanium dioxide, layered oxynitrides, and oxyhalides have been found to show promise as new visible-light responsive photocatalysts. In addition, some anion-doped oxides have also been found to be effective as secondary battery materials. Furthermore, in the creation of phosphor materials, the excitation and emission wavelengths can be tuned by band control through anion mixing. The nanoarchitectonics of functional mixed anion compounds has the potential to create a group of functional materials with design guidelines that break with conventional wisdom.

Although atoms are the most basic building blocks of matter, it has become possible to collect and assemble them according to their purpose. Such manipulations have led to the development of high-entropy alloys and multi-element quantum dots that exhibit more highly functional properties. It is also possible to tune dopants in solid electrolytes to create groups of

(A) Highly Strained Nonplanar Aromatic Hydrocarbons

Carbon Nanobelt　　Warped Nanographene　　Multiple Helicene　　All-Benzene Trefoil Knot

(B) Fold-in Oxidative Fusion Reaction

Fold-in Oxidative Fusion
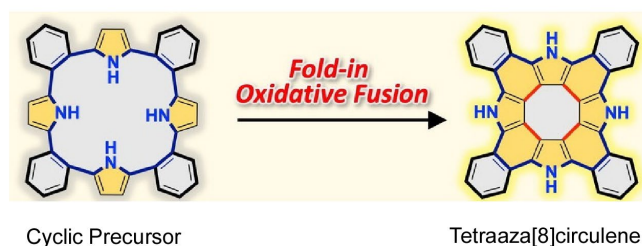
Cyclic Precursor　　　　　　　　Tetraaza[8]circulene

Figure 4. (A) Highly strained nonplanar aromatic hydrocarbons (carbon nanobelt, warped nanographene, multiple helicene, and all-benzene trefoil knot). (B) Fold-in oxidative fusion reactions of cyclic precursors containing pyrrole for novel heterocyclene. Reproduced with permission.[47, 48] Copyright 2022, Chemical Society of Japan.

materials with discrete electrical properties. The concept of mixed anions also makes it possible to design materials that break with conventional wisdom. These examples show that even at the most basic level of atomistic nanoarchitectonics, such as collecting atoms or combining elements, it is possible to create a wide variety of functional materials.

3. Molecular Nanoarchitectonics

Along with atoms, molecules are the building blocks of matter. Various functional materials are created by nanoarchitectonics, which links or assembles molecular units. What must be considered at a more fundamental level is molecular nanoarchitectonics, which is the formation of the molecules themselves. There are two major approaches to molecular nanoarchitectonics. One approach is based on authorized organic synthesis.[42] Organic chemistry and organic synthesis have a long history, and the synthesis of many molecules has already been accomplished. However, even with that history, not everything has been achieved. There is still room for challenges in molecular nanoarchitectonics based on organic synthesis, such as the synthesis of molecules with topological specificity.[43] In contrast, what has emerged in recent years is a coupling technique between nanotechnology and organic synthesis. Local probe chemistry[44] has been proposed as an organic synthesis method that uses the tip of a STM, a key tool in nanotechnology. This is like using a tip to pick up a reactant and press it to a specific section of another molecule for an addition reaction. The stimulation from the tip can also induce a polymerization reaction with a diacetylene monomer laid down on the surface from a specific location.[45] These molecular syntheses are distinct from conventional organic synthesis, which is determined by thermodynamics and other factors. In addition, reports of on-surface synthesis,[46] in which reactions on the substrate surface are observed by STM, have become active. In this section, examples of molecular nanoarchitectonics, in which molecules are created, will be selected from these trends and discussed.

As molecular nanoarchitectonics based on organic chemistry, Segawa summarized the synthesis of highly strained nonplanar aromatic hydrocarbons in a recent review (Figure 4A).[47] Possible nonplanar aromatic hydrocarbons include cyclic arenes, banded arenes, distorted arenes, helical arenes, and topologically unique arenes. Such attempts would produce a variety of topological structures in addition to nanocarbon substructures. Those novel molecules are expected to have a wide range of applications, such as semiconductors, light-emitting devices, bio-imaging, and pharmaceuticals. Accordingly, the chemistry of nonplanar aromatic hydrocarbons is expected to develop at an accelerated pace. Solid-state structure design of nonplanar aromatic hydrocarbons remains challenging. In addition to these molecular synthesis nanoarchitectonics, the methodology of nanoarchitectonics of three-dimensional molecular assemblies by π-π stacking and covalent bonding could significantly change the materials science of aromatic molecules.

As for aromatic molecular nanoarchitectonics, Tanaka summarized fold-in oxidative fusion reactions in a recent review article.[48] The fold-in oxidative fusion reaction of heteroaromatic necklace-like molecules is a promising method to obtain circulenes and helicenes encapsulating heteroatoms. Design of precursors for intramolecular oxidative coupling is the key to construct novel polycyclic compounds. For example, as shown in Figure 4B, fold-in oxidative fusion reactions of cyclic precursors containing pyrrole and thiophene yield novel heterocyclenes and heterohelicenes. The development of fold-in oxidative fusion reactions also allows the synthesis of novel hetero[8]circlenes, pentaaza[10]circlenes, and heterohelicenes in reasonable yields. In particular, multivalent hetero[n]circlenes are also attractive targets in terms of aromaticity variation and electrochromic behavior. These molecular nanoarchitectonics are expected to be extended to materials science of novel hetero-nanographenes, etc.

In addition to the further development of molecular nanoarchitectonics through organic chemistry as described
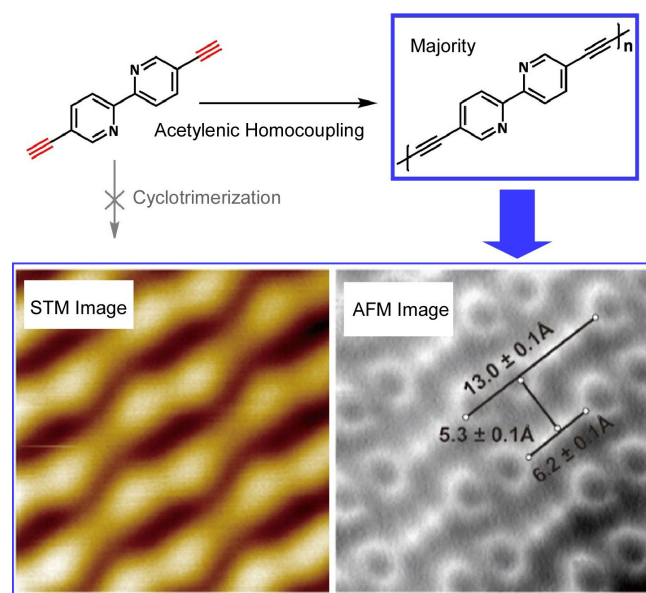
Figure 5. Acetylene homocoupling reaction of polar terminal alkynes on Au(111) upon observations with using bond-resolved scanning probe microscopy. Reproduced with permission.[49] Copyright 2023, American Chemical Society.

above, there has been a growing number of attempts to architect molecules on solid substrates using a combination of nanotechnological observation techniques. This series of studies is referred to as on-surface synthesis. A typical example of such an attempt is the construction of carbon nanostructures with sp hybridization through acetylene homocoupling at the surface. However, tactics to increase the efficiency of linear acetylene couplings are not well established. In contrast, Björk, Zhang, Chi, and co-workers investigated the acetylene homocoupling reaction of polar terminal alkynes on Au(111) using bond-resolved scanning probe microscopy (Figure 5).[49] Substitution

of benzene for pyridine significantly inhibits the cyclic trimerization pathway. In particular, the pyridine nitrogen modification significantly alters the coupling motif in the initial C-C coupling step (head-to-head, head-to-tail, etc.). This favors linear coupling over cyclotrimerization. As a result, linear coupling is facilitated and aligned *N*-doped grapyridine nanowires are produced. The pyridine N-doped graphdiyne nanowires produced are expected to have high catalytic performance, but the details are not well understood. In particular, nanoarchitectonics of the electrode/catalyst interface in the surface-synthesized graphdiyne nanowire system to
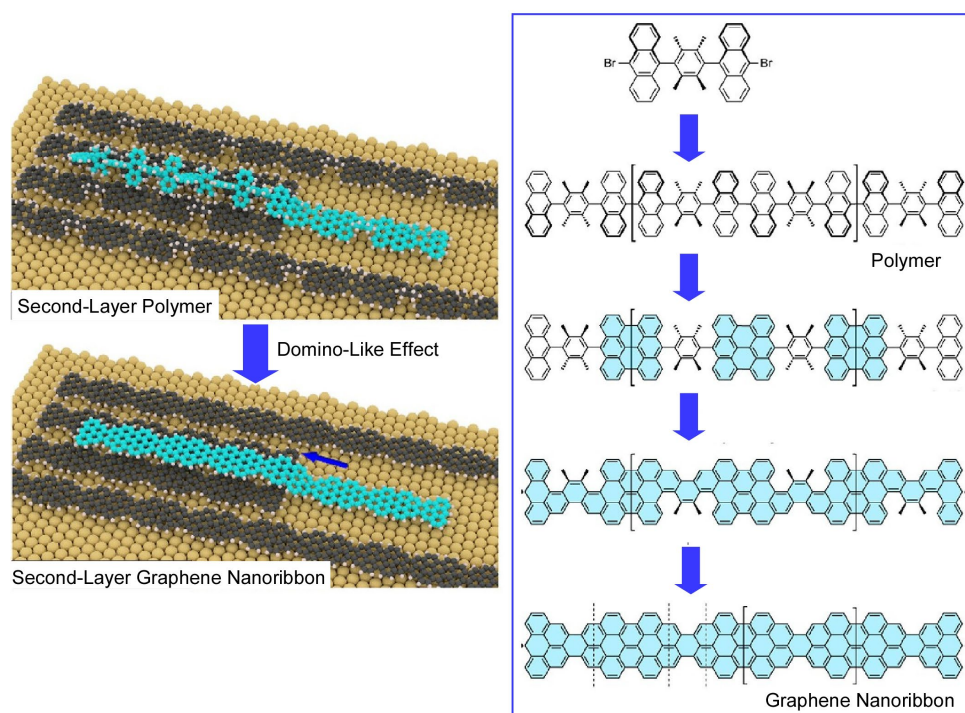

Figure 6. Topologically non-trivial graphene nanoribbons grown directly via multi-step coupling in the second layer as well as in the surface layer. Reproduced with permission.[50] Copyright 2023, American Chemical Society.
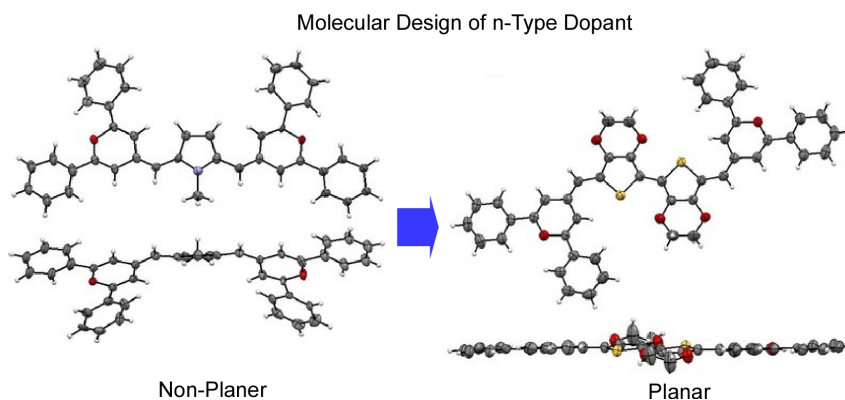
Molecular Design of n-Type Dopant

Non-Planer

Planar

Figure 7. Molecular structures of dopants with non-planar and planar conformations. Reproduced with permission.[51] Copyright 2022, Chemical Society of Japan.

investigate the effect of doped atoms on the catalytic process will provide a powerful guide for the design of precise catalytic molecules.

Molecular nanoarchitectonics in multilayered structures, rather than on a single surface layer, has also been investigated by Ma, Tan, Wang and co-workers. examined (Figure 6).[50] In this case, topologically non-trivial graphene nanoribbons were grown directly via multi-step coupling in the second layer as well as in the surface layer. After sequential annealing at 700 K and 780 K, second layer topological graphene nanoribbons covalently bonded to the first layer were obtained. This molecular design minimized local steric hindrance of the precursor. It is suggested that the second layer graphene nanoribbon undergoes a domino-type cyclic hydrogenation reaction that is remotely triggered at the linkage. A structure-strain mechanism of multi-step cyclodehydrogenation reactions combines domino-like effects and successive couplings. It was confirmed that highly tunable Kondo resonances from the quasiparticle gap of the topological band and the topological terminal spin are obtained in the nanoarchitectonically high-quality second-layer graphene nanoribbons. The obtained results pave the way for a variety of multilayer graphene nanostructures in which quantum spins and topological states can be designed. This is a useful insight for quantum computing and quantum sensing.

Proper molecular nanoarchitectonics to create the desired electronic states is also important. Electron doping is an essential process for the development of n-type organic thermoelectric materials. The importance of searching for efficient n-type dopants is also an important target in molecular

nanoarchitectonics. Takimiya and co-workers have synthesized and characterized new candidate molecules as n-type dopants (Figure 7).[51] The electron doping ability is highly dependent on the molecular conformation in the solid state. In their design, planar molecules consisting of 2,2'-bis(3,4-ethylenedioxythiophene) moieties can be doped into poly(benzimidazobenzophenanthroline). Conformational considerations suggest that the planarity of their dopant molecules improves their electron doping ability. The findings obtained here may provide useful information for the molecular design of superior n-type dopants in the development of organic thermoelectric applications.

Molecular nanoarchitectonics, the architecture of molecules themselves, is undoubtedly important. As a development of organic synthesis, which has a long and uninterrupted history, the challenge is to synthesize topologically specific molecules. By considering the conformation of such synthesized molecules, the design of molecules with better properties can be elucidated. Furthermore, nanotechnology-based molecular observation techniques have led to a detailed elucidation of the principles and behavior of molecular nanoarchitectonics. They will become the technical system necessary to architect structures that are optimized at the molecular level for the desired properties.

4. Supramolecular Nanoarchitectonics

In terms of size, a larger target than atoms, clusters, and molecules is the functional structure in which they assemble. In many cases, unit molecules form self-assembled structures through supramolecular nanoarchitectonics to achieve new
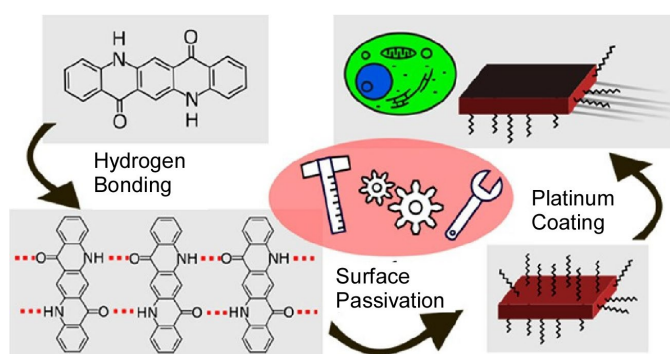

Figure 8. Organic pigment-based Janus microrobots based on hydrogen bonding with entering capability into cells. Reproduced with permission.[54] Copyright 2023, American Chemical Society.
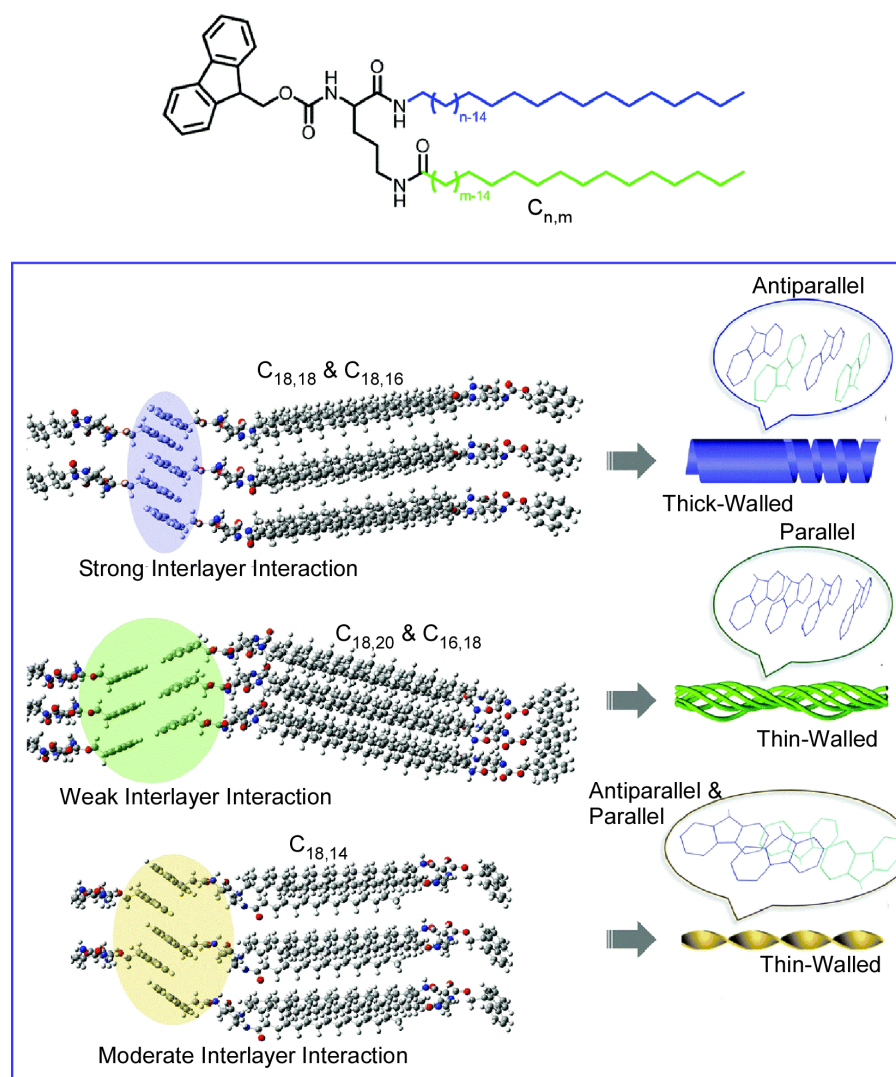
Figure 9. Self-assembled structures of several Fmoc-protected ornithine lipids with asymmetric alkyl tails (nanotubes to bundles, nanotwists, and so on). Reproduced with permission.[55] Copyright 2022, Royal Society of Chemistry.

functions.[52] Such attempts have been widely made in supramolecular chemistry and related materials chemistry.[53] Since it is impossible to give an exhaustive description of them here, this article will pursue their possibilities with a few characteristic recent examples.

Supramolecular nanoarchitectonics can be used to assemble highly functional objects such as microrobots. Autonomous microrobots are at the forefront of biomedical research. It is expected that microrobots will be able to accomplish specific tasks at the intracellular level. Pumera and co-workers report on the nanoarchitectonics of microrobots using the organic pigments quinacridone and indigo (Figure 8).[54] The introduction of protecting groups into these pigments prevents hydrogen bonding of the pigment molecules, making them soluble in organic solvents. This allows nanoarchitectonics into microparticles in solution by hot injection. The microrobots were fabricated by asymmetric deposition of platinum on these dye particles. These nanoarchitectonized microrobots are capable of autonomous movement in the presence of hydrogen peroxide. Furthermore, the microrobots were examined in the presence of mouse colon cancer cells and were found to internalize into the cells. Their ability to internalize into cancer cells was not affected by the presence of platinum. These examples demonstrate the potential for fabricating organic dye-

based microrobots for biomedical applications by using the principles of nanoarchitectonics. There is also the possibility of decorating organic dyes with biomolecules and utilizing their original photoelectrochemical activity for function. Such a nanoarchitectonics approach could also add various additional functionalities to microrobots for biomedical applications.

In supramolecular nanoarchitectonics, the shape of the aggregates formed depends on subtle differences in the structure of the unit molecules. For example, it is of interest from a biological point of view how lipid molecules form aggregate structures depending on their original molecular structure. As is often the case in natural lipid structures, asymmetric tails in a single lipid molecule are expected to influence the structure and properties of the aggregate. As a model, Zhu, Liu, and co-workers investigated the self-assembly behavior of artificial building blocks composed of asymmetric tail portions (Figure 9).[55] Several Fmoc-protected ornithine lipids with asymmetric alkyl tails were synthesized and their assembly structures were investigated. Depending on the asymmetry of the two tails, the assembly structure was found to change from nanotubes to bundles, nanotwists, and so on. The mode of interaction is controlled by van der Waals interactions between alkyl tails, π-π stacking between Fmoc motifs, and hydrogen bonds formed by three amide bonds in the lipid bilayer. The asymmetry of the lipid
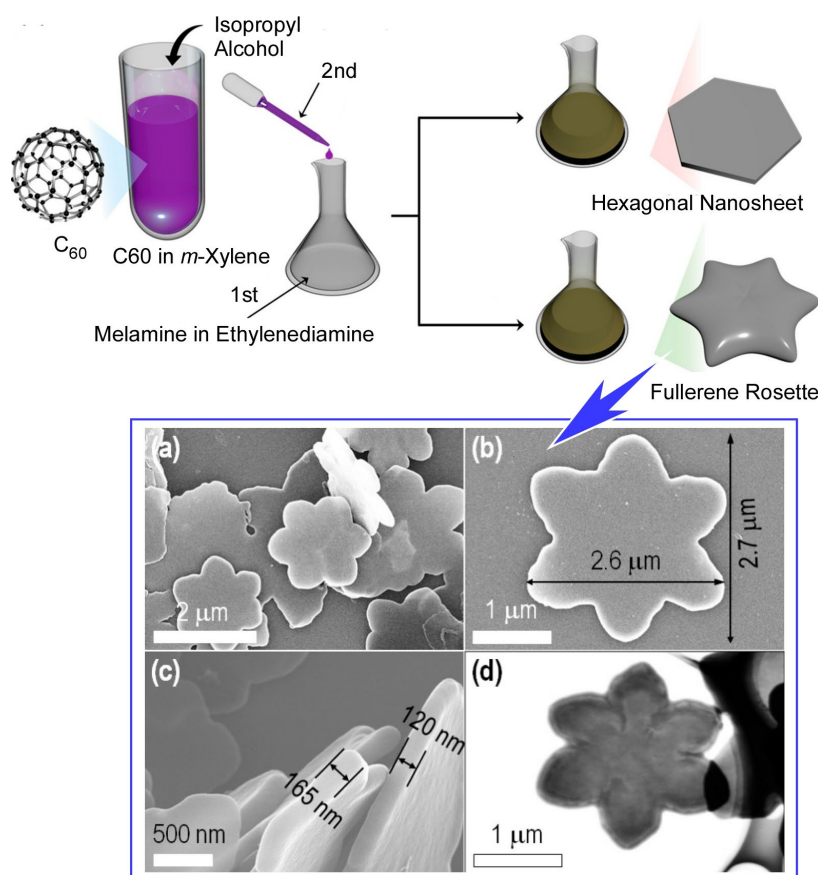
Figure 10. Self-assembly processes involving in situ reactions of C_{60} molecules with melamine/ethylenediamine components in solution to provide a new type of two-dimensional structure, aggregate was obtained, fullerene rosette. Reproduced under terms of the CC-BY license.[60] Copyright 2022, Guoping Chen, Biswa Nath Bhadra, Linawati Sutrisno, Lok Kumar Shrestha, and Katsuhiko Ariga, published by [MDPI].

tails causes an imbalance between inter- or intralayer π-π stacking and hydrogen bonding and van der Waals interactions, resulting in various interaction modes. These studies provide some insight into understanding the association behavior of lipids in biological systems due to their asymmetric structures, and are also useful for the design of various functional materials. For example, they may provide new strategies for the rational design of supramolecular chiral luminescent materials. New strategies for rationally modulating the chiral and luminescent properties of supramolecular materials may be established, such as methods for utilizing such strategies in tunable circularly polarized luminescence materials.

As described above, the morphology of an aggregate can be controlled by subtle changes in the structure of the molecule. In other cases, very simple molecules can give rise to extremely diverse forms of aggregation. For example, the aggregation of fullerene molecules (C_{60}, C_{70}), which are single-element, zero-dimensional molecules, can form one-dimensional,[56] two-dimensional,[57] three-dimensional,[58] and hierarchically structured[59] assemblies. The potential of supramolecular nanoarchitectonics is that simple unit units can generate various morphological concepts. Recently, Chen et al. investigated self-assembly processes involving in situ reactions of C_{60} molecules with melamine/ethylenediamine components in solution (Figure 10).[60] As a result, a new type of aggregate was obtained, the fullerene rosette, which is a micron-sized two-dimensional amorphous shape-regular body. The melamine/ethylenediamine component in the fullerene rosette was suggested to be

covalently bonded to the fullerene. The internal structure of the rosettes was found to have a unit-layered structure that roughly corresponds to an interdigitated fullerene bilayer or a monolayer of modified fullerene molecules. The melamine/ethylenediamine component in the fullerene rosette was suggested to be covalently bound to the fullerene. The internal structure of the rosettes was found to have a unit-layered structure that roughly corresponds to an interdigitated fullerene bilayer or a monolayer of modified fullerene molecules. Fullerene rosettes are the result of the accumulation of such bilayer/monolayer assemblies of low-crystalline, hybridized fullerenes. Overall, the structure of the fullerene rosette has a two-dimensional nature. This flat shape is advantageous for immobilization on device surfaces such as electrodes. Sensors coated with fullerene rosettes on the electrode surface of a quartz crystal resonator (QCM) are capable of sensitively detecting a target simply by exposure to the target vapor. A portable volatile organic compound sensing device can be developed. In fact, a prototype sensor system with fullerene rosettes immobilized on a QCM surface was fabricated to demonstrate selective sensing of formic acid. As a guest sensitivity comparison, large values were obtained for basic (formic acid/pyridine > 30) or aromatic (formic acid/toluene > 110) guests. The covalent incorporation of the melamine/ethylenediamine component of the fullerene rosette and the inclusion of a multilayer-like nanostructure are thought to be responsible for the high selectivity for formic acid.

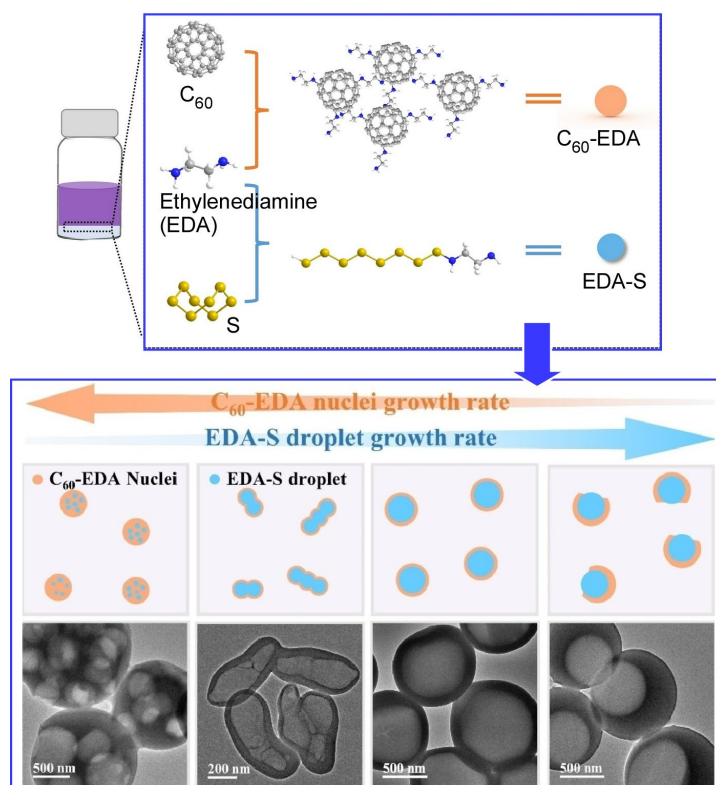Nanomaterials with hollow structures are expected to perform various functions in materials engineering.[61]

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Figure 11. Preparation of fullerene (C$_{60}$) assemblies with different hollow structures using a kinetically controlled liquid-liquid interface precipitation method. Reproduced with permission.[62] Copyright 2022, Wiley-VCH.

Nanoarchitectonics is also an attractive target to freely create such hollow structures. Chen et al. have successfully synthesized fullerene (C$_{60}$) assemblies with different hollow structures using a kinetically controlled liquid-liquid interface precipitation method (Figure 11).[62] In this attempt, a C$_{60}$-ethylenediamine shell was first formed using 1,2-ethylenediamine as a covalent cross-linker for C$_{60}$ molecules. Simultaneously, in-situ generated ethylenediamine-sulfur droplets were applied as an egg yolk. Removal by washing after formation of the egg yolk-shell structure yields a hollow structure. By controlling the kinetics of C$_{60}$-ethylenediamine nucleation and template ethylenediamine-S growth, a variety of structures can be formed by a kinetically controlled liquid-liquid interfacial deposition method. During structure formation, ethylenediamine-S droplets diffuse and collide due to Brownian motion and hydrophobic effects, while C$_{60}$-ethylenediamine nuclei aggregate on the surface of ethylenediamine-S droplets. The growth rates of C$_{60}$-ethylenediamine nuclei and ethylenediamine-S droplets are balanced to control the synthesis of various hollow structures. Indeed, porous spheres, string-like hollow spheres, hollow spheres, and open-aperture hollow spheres were obtained. This supramolecular nanoarchitectonics approach allows the synthesis of a variety of morphologies, including solid spheres with tunable size and hollow spheres with tunable pores and
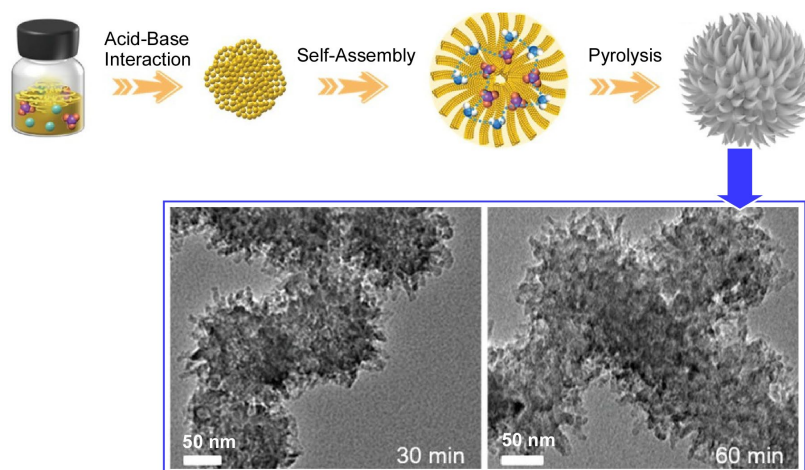

Figure 12. Fabrication of carbon nanostructures with high zinc affinity and stability for Zn ion storage with high supercapacitor activity and durability through Lewis acid and base interaction, self-assembly, and pyrolysis. Reproduced with permission.[63] Copyright 2022, Wiley-VCH.
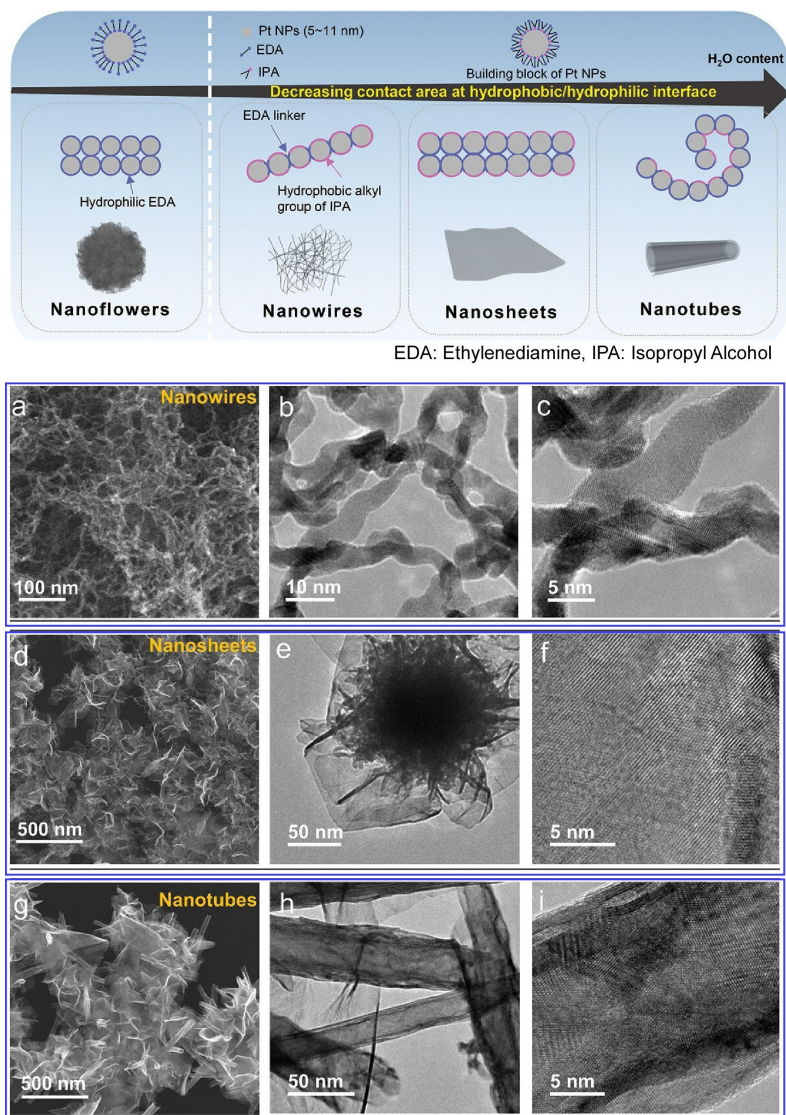
Figure 13. A method to produce platinum particles in the form of nanoflowers, nanowires, nanotubes, etc. by chemical reduction of platinum under a delicate combination of ethylene diamine, isopropyl alcohol, and water. Reproduced under terms of the CC-BY license.[65] Copyright 2022, Guoping Chen, Santosh K. Singh, Kotaro Takeyasu, Jonathan P. Hill, Junji Nakamura and Katsuhiko Ariga, published by [Taylor & Francis].

cavities. These resulting C$_{60}$ hollow materials could be materials for carbon materials for a variety of advanced applications.

Structures fabricated by supramolecular nanoarchitectonics are expected to exhibit a variety of functions. Applications in energy-related fields are a promising outlet. For example, carbon nanostructures with high zinc affinity and stability are useful for Zn ion storage with high supercapacitor activity and durability as reported by Liu and co-workers (Figure 12).[63] In their approach, a Lewis acid (ferric chloride) and a base (p-phenylenedimethanol) can interact to form organic nanoparticle modules. They self-assemble into superstructures constructed from nanotentacle building blocks via hydrogen bonding and π-π stacking. The designed carbon superstructure is beneficial as a cathode for aqueous Zn-ion capacitors. The superstructure has an exposed electrosorption platform and a pro-zinc heterodiatomic pyridine/carbonyl motif. Based on this structural property, highly kinetic ion transfer activation and robust electrochemical reactions are facilitated. The created Zn-

ion hybrid capacitors exhibit excellent energy and power output, high current persistence, and long ultra-stable cycle life. This nanoarchitectonics strategy opens new possibilities for customizing high-performance carbon superstructures.

In supramolecular nanoarchitectonics, various structures are created by assembling and organizing unit molecules. The morphology of the assembled structures can be controlled in various ways by the subtle structural differences of the unit molecules. Even with single-element, zero-dimensional units such as fullerenes, the assembly structure can be freely modified by tuning the reactions and kinetics of the assembly process. The resulting structures are expected to have many functions, ranging from advanced nano-functions such as micro-motors to practical applications such as sensing and energy applications. The examples given here are only a limited number of examples, and a wide variety of functions have been reported for the products of supramolecular nanoarchitectonics.
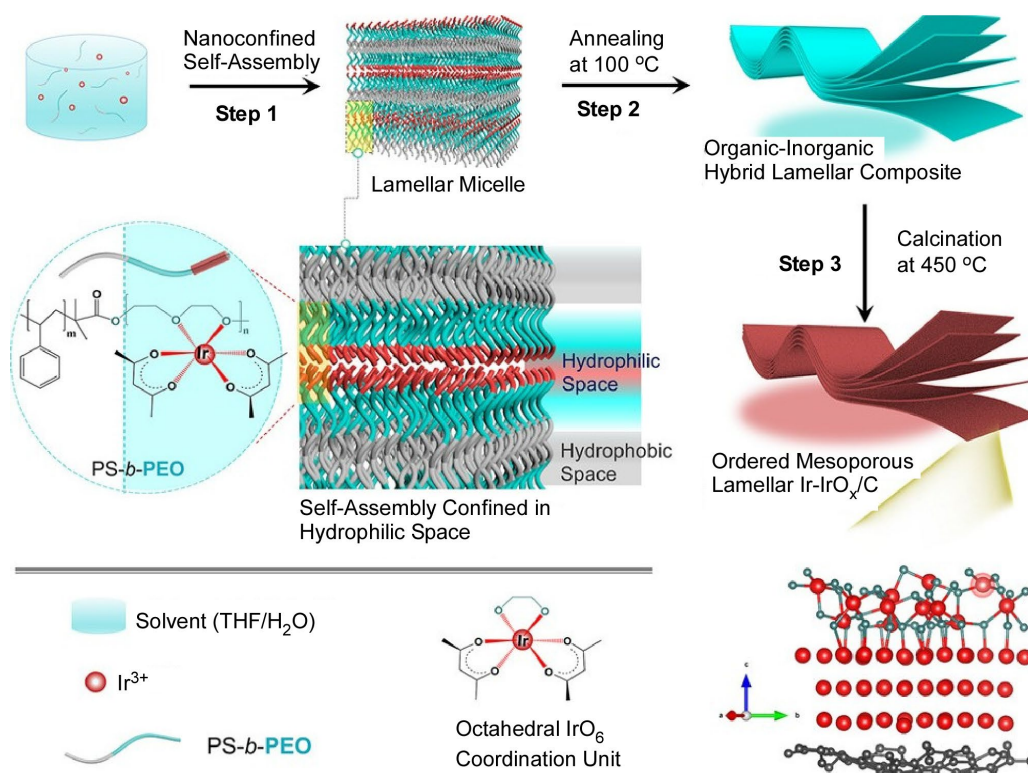
Figure 14. Fabrication of ultrathin Ir-IrOx/C nanosheets with ordered interlayer spacesfor facile oxygen-evolving reactions through nanoconfined self-assembly, calcination etc. Reproduced with permission.[66] Copyright 2022, American Chemical Society.

5. Inorganic Nanoarchitectonics

Architecting functional structures from unit structures is not limited to supramolecular organization of organic molecules. The nanoarchitectonics of inorganic materials that weave together clusters and nanomaterials has also been extensively studied.[64] There are many examples of this classification as well, and it is impossible to give an exhaustive description, so the section will discuss a few recent examples and extract their characteristics.

Platinum (Pt) is an important catalyst for oxygen reduction reactions, but its electrocatalytic activity is strongly dependent on the morphology of platinum. In order to unravel the morphology of Pt with appropriate activity, inorganic nanoarchitectonics is important to produce various forms of Pt materials. Chen et al have developed a method to produce platinum particles in the form of nanoflowers, nanowires, nanotubes, etc. by chemical reduction of platinum under a delicate combination of ethylene diamine, isopropyl alcohol, and water (Figure 13).[65] In this methodology, NaBH4 is used as a reducing agent to rapidly form Pt nanoparticles. Aggregation is then promoted by the addition of ethylenediamine. The adsorption of ethylenediamine molecules stabilizes the Pt nanoparticles in solution and increases the hydrophilicity of the Pt nanoparticles. The presence of two amino groups can also link the Pt nanoparticles. The sheet structure observed in the Pt nanoflowers as a constituent structure may be due to the minimization of surface energy by increasing the interfacial area. This Pt nanoparticle assembly morphology can be easily controlled by tuning the hydrophobic/hydrophilic interactions by adding isopropanol and H_2O. Since the surface hydrophobicity of Pt nanoparticles is increased compared to Pt-ethylenediamine species, nanowires, nanosheets, nanotubes, and nanotubes can be

formed by simply changing the H_2O content. The morphology of Pt nanoparticle aggregates changes just by changing the H_2O content. This is a result of the reduced contact area of the H_2O solvent. Similarly, the formation of Pt nanotubes derived from nanosheets that curl as H_2O content increases can also be explained. The Pt nanoparticles prepared here showed better oxygen reduction reaction activity than Pt black. This is the effect of their hierarchical structures. Among them, Pt nanotubes showed the highest oxygen reduction reaction catalytic activity in acidic electrolytes. These results establish a nanoarchitectonics methodology for building hierarchical morphologies of Pt using Pt nanoparticles as building blocks.

Iridium-based electrocatalysts are promising materials for acidic oxygen evolution reactions. Inorganic nanoarchitectonics for high performance has been investigated. Li, Yu, Zhao, and co-workers reported a nanoconfined self-assembly strategy using block copolymers forming stable end-confined lamellar micelles.[66] Ultrathin Ir-IrOx/C nanosheets with ordered interlayer spaces were synthesized to facilitate oxygen-evolving reactions (Figure 14). First, a liquid-liquid microphase separation of the different components occurs due to evaporation of tetrahydrofuran. The block copolymer, iridium precursor, and acetylacetonate undergo nanoconfined self-assembly. These processes result in the formation of lamellar organic-inorganic composite micelles. Continuous evaporation of the residual tetrahydrofuran and water at 100 °C yields an organic-inorganic iridium composite. Further calcination in an argon atmosphere forms an ordered mesoporous Ir-IrOx/C catalyst. The mixed valence state and the O(II-δ) moiety of the two-dimensional mesoporous Ir-IrOx/C were found to be the active species in the oxygen-evolving reaction by experimental and theoretical approaches. Here, the adsorption free energies of the oxygen-
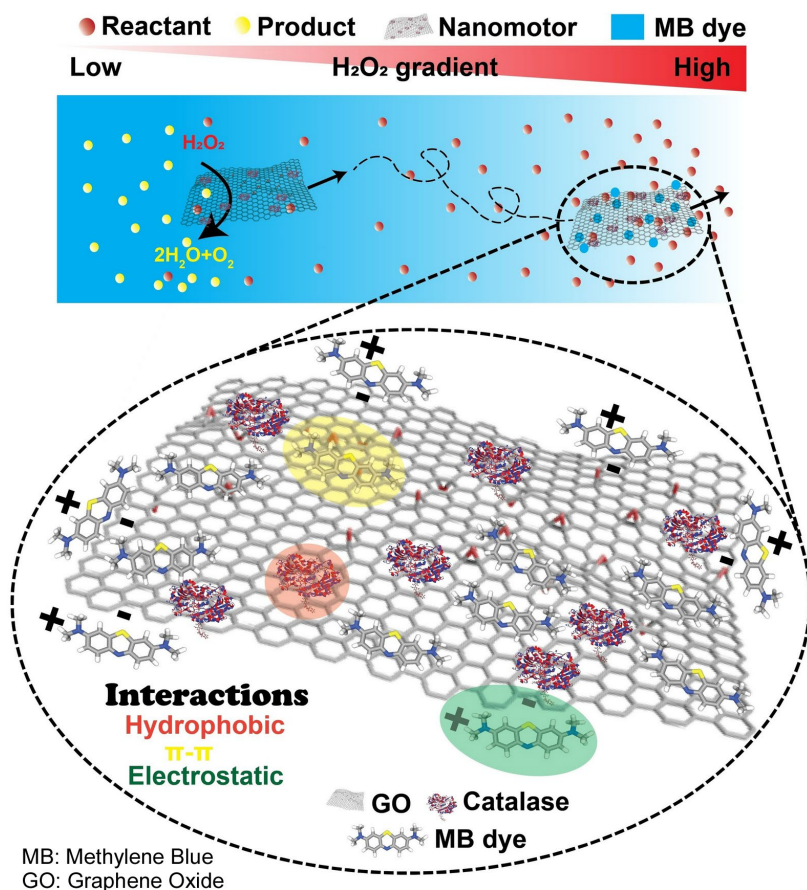
Figure 15. Soft strategy for an enzyme-powered two-dimensional nanobot that achieves active motion at very low fuel concentrations through non-covalent nanoarchitectonics on graphene oxide. Reproduced with permission.[67] Copyright 2021, Wiley-VCH.

containing intermediates are balanced. Through the synthesis of catalysts with ordered mesoporous interlayer spaces, the origin of the high activity of iridium-based electrocatalysts for oxygen-evolving reactions is revealed. This nanoarchitectonics strategy paves the way for the design of high-performance two-dimensional ordered mesoporous electrocatalysts.

Mathesh et al. developed an enzyme-powered two-dimensional nanobot that achieves active motion at very low fuel concentrations (0.003 % H_2O_2) by a simple strategy based on soft nano-architectonics (Figure 15).[67] The two-dimensional nanobots were fabricated by non-covalent nanoarchitectonics based on graphene oxide. The nanobots exhibited efficient positive chemotaxis. The velocity of the two-dimensional nanobots increased with increasing fuel concentration and decreased with time. Therefore, the chemotaxis behavior was based on the fuel gradient. Furthermore, due to the buoyancy of the solute, the two-dimensional nanobots showed the ability to swim against gravity. As part of these capabilities of two-dimensional bots, a proof-of-concept study of environmental remediation without the need for external forces was conducted. Specifically, the two-dimensional nanobots were able to remove methylene blue dye in situ with 85% efficiency. Two-dimensional nanobots have a wide range of potential applications ranging from biomedical to plant nanobiotechnology. To meet those demands, it is important to design and develop nanobots with the necessary capabilities through nanoarchitectonics.

In living systems, tissues composed of tightly packed cell arrays act as sheet-like biosynthetic factories. Individual cells are microreactors working in a highly viscous and confined environment. As a mimic of such structures, Cheng and co-workers have nanoarchitectonized a similar sheet-like chemical synthesis factory for the synthesis of novel nanocrystals (Figure 16).[68] This is a soft polystyrene-encapsulated nanoframe reactor array. It acts as a chemical plant for synthesizing a series of new nanocrystals that are difficult to achieve with conventional bulk solution-based strategies. The volume of the individual reactors fits the zeptolitre range. Within them is a uniquely confined environment that allows for directional inward crystallization that differs from that of bulk solutions. As a result, products are obtained that are difficult to achieve in ordinary systems based on bulk solutions. Nanocrystals of mono-, bi-, tri-metallic, and even semiconducting materials with tunable internal structures can be generated. The developed reactor array was resilient and robust, allowing the structural integrity of the nanocrystals to be maintained during the crystallization process. It is possible to control both the overall morphology of the nanocrystals and their internal structure by fine-tuning parameters during the nucleation process. It is hoped that this concept of nanoreactor chemical synthesis will provide an opportunity to open new routes for designing countless other nanocrystals, which will be applied in fields such as sensing, energy, and optoelectronics.

Nanoarchitectonics of inorganic materials can be performed using metal atoms and nanomaterials as units. Compared to organic molecules, inorganic materials are composed of many types of elements, and the functions they exhibit are diverse. Therefore, the structure formed has a large effect on the efficiency of the function. As shown above, many
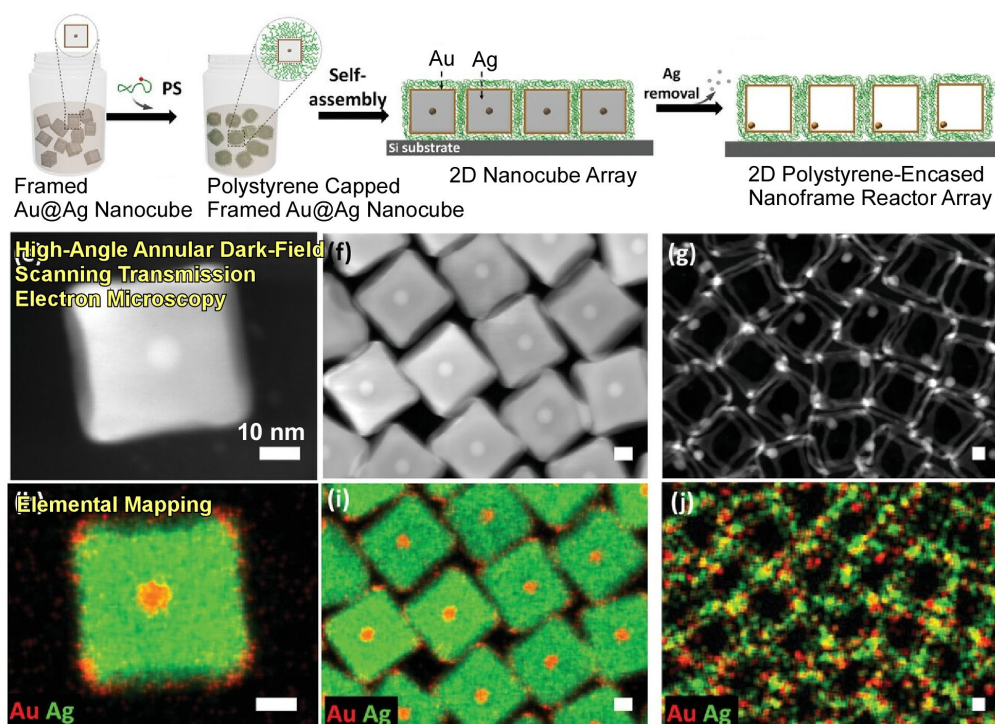
Figure 16. Sheet-like chemical synthesis factory for the synthesis of novel nanocrystals, a soft polystyrene-encapsulated nanoframe reactor array: fabrication strategies and images. Reproduced with permission.[68] Copyright 2021, Wiley-VCH.

application studies have been conducted mainly in energy-related technologies, and control of nanostructures is essential for highly efficient functional expression, and inorganic nanoarchitectonics plays a significant role.

6. Biomolecular Nanoarchitectonics

One goal of nanoarchitectonics is to develop advanced functional systems that are comparable to biofunctional systems.[69] In a biofunctional system, many biomolecules are assembled and organized to construct a rational functional system. There are many attempts to architect highly functional systems using biomolecules or molecules that mimic them.[70] Recent examples of such biomolecular nanoarchitectonics are listed below.

Peptides are a prime example of useful constituent units of nanoarchitectonics.[71] Aggregates and organizations of peptides give rise to a wide variety of structures according to defined hydrogen bonding motifs. There are also many attempts to immobilize functional species within such organizational structures. For example, designer peptidomimetics, in which metal ions are immobilized within peptide organizers and multiple chemical transformations are achieved by modulating the metal oxidation state, has also received much attention. Govindaraju and coworkers achieved it by copper chelation and self-assembly of amyloid β-peptides.[72] In this case, thermodynamically stable nanosheets and kinetically controlled micelle-like structures are formed. Upon addition of Cu^{II}, the peptide fibrils first self-assemble into nanosheets. Further, continuous addition of Cu^{II} results in the formation of micelle-like core-shell structures. These nanosheet and micelle-like structures differentially stabilize the Cu^I and Cu^{II} states, respectively. This heterogeneous metal-anchored structure can catalyze tandem oxidative hydrolysis and alkyne-azide cycloaddition reactions. This attempt at biomolecular nanoarchitectonics provides a strategy for designing artificial biocatalytic structures capable of performing multiple chemical transformations. Metal complex structures that can successfully utilize different oxidation states may also be useful in understanding the complex redox activities of metalloproteins.

Actively functioning nano-micro objects can also be constructed by hybrid nanoarchitectonics of nanomaterials and biomolecules. An example is bio-inspired nanomotors that exhibit effective propulsion and load carrying capabilities. Multifunctional nanomotors have attracted a great deal of attention due to their potential for biomedical applications. Díez, Mira, Martínez-Máñez, and co-workers reported the design and application of multifunctional gated Janus platinum-mesoporous silica nanomotors (Figure 17).[73] The Janus structure consists of a propulsion element, a Pt nanodendrite, and mesoporous silica nanoparticles, which are drug-filled nanocontainers capped with a β-cyclodextrin-modified ficin enzyme. The nanomotor Janus structures with these nanoparticles were made according to a synthetic method conjugated to an anisotropic nanodevice. Specifically, an interfacial environment was used. Both nanoparticles were linked at the interface of a Pickering emulsion formed by paraffin wax and water-ethanol. The nanoarchitectonized active nanoparticles can penetrate the extracellular polymer matrix and reach the deeper layers of the biofilm. The nanomotors are capable of self-propelled motion driven by H_2O_2 and hydrolysis of the extracellular polymer matrix of the biofilm by ficin. Furthermore, they effectively destroy bacterial biofilms via pH-triggered release of vancomycin. The function of the nanomotor synergistic antimicrobial activity was demonstrated in the removal of Staphylococcus aureus biofilms. Such nanomotors powered by low concentrations of H_2O_2 have potential applications in specific microenvironments. Examples include the inflammatory response of wounds and infections caused by the
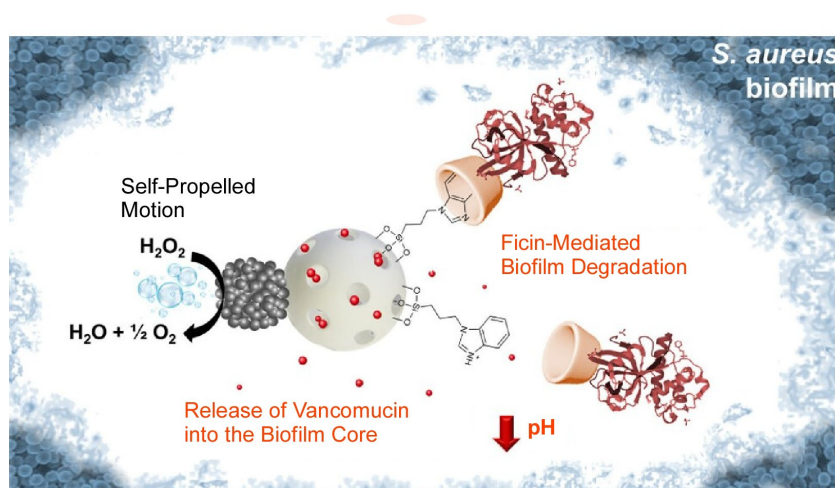
Figure 17. Multifunctional gated Janus platinum-mesoporous silica nanomotors consists of a propulsion element, a Pt nanodendrite, and mesoporous silica nanoparticles, which are drug-filled nanocontainers capped with a β-cyclodextrin-modified ficin enzyme. Reproduced under terms of the CC-BY license.[73] Copyright 2023, Miglė Žiemytė, Andrea Escudero, Paula Díez, María D. Ferrer, Jose R. Murguía, Vicente Martí-Centelles, Alex Mira, and Ramón Martínez-Máñez, published by [American Chemical Society].

presence of H_2O_2-producing lactic acid bacteria. This, hybrid. The design of nanomotors by nanoarchitectonics is very versatile and has potential applications in the treatment of biofilms of various species.

Photodynamic therapy is a promising treatment for cancer. There have been nanoarchitectonics attempts using biomolecules to create structures that perform this function. Danielli, Calvaresi, and coworkers used a genetic and chemical orthogonal nanoarchitectonics approach to create M13 bacteriophage as a targeted vector for efficient photodynamic killing of cancer cells (Figure 18).[74] M13 was genetically engineered to display a peptide that binds to the epidermal growth factor receptor on the phage tip. In addition, hundreds of Rose Bengal photosensitizing molecules were bound to the capsid surface. The phage displayed EGFR-targeting tropism and was internalized by A431 cancer cells overexpressing the epidermal growth factor receptor. Upon internalization, the

phage Rose Bengal derivative generated intracellular reactive oxygen species and was activated by ultra-low intensity white light irradiation. The nanoarchitectonics of the phage produced cancer cell killing activity at picomolar concentrations of phage. The nanoarchitectonics approach developed here has already been approved for clinical application or is in clinical trials. Given that several photosensitizers acting in various diagnostic windows can be readily conjugated to the phage capsid, bae more applications can be expected.

Cells recognize multiple physical and chemical cues at the boundary region between the cell lipid membrane and the extracellular matrix and respond molecularly. This leads to the expression of various functions. Mimicking such microenvironments is an excellent target for biomolecular nanoarchitectonics. Fakhrullin, Volodkin, and co-workers have developed a lipid bilayer supported on a soft biopolymeric multilayer cushion to mimic the cellular interfacial environment
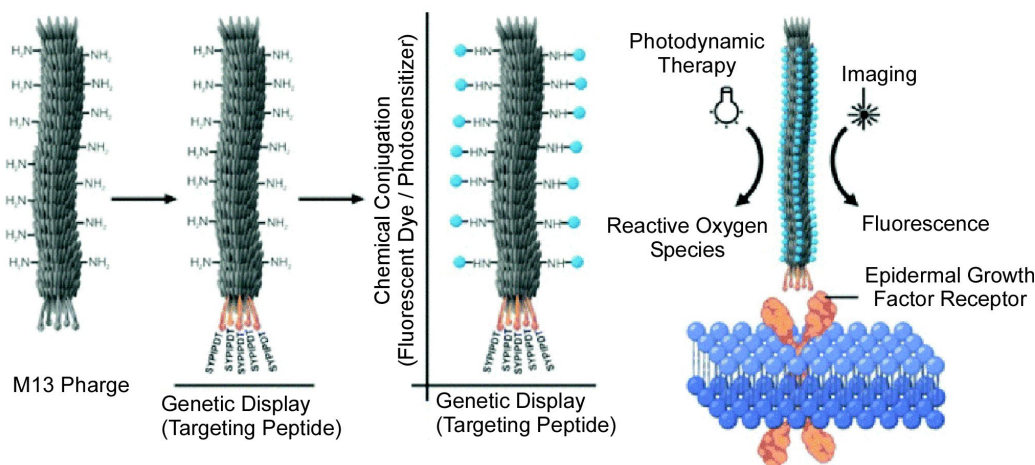

Figure 18. Genetic and chemical orthogonal nanoarchitectonics approach to create M13 bacteriophage as a targeted vector for efficient photodynamic killing of cancer cells. Reproduced with permission.[74] Copyright 2022, Royal Society of Chemistry.
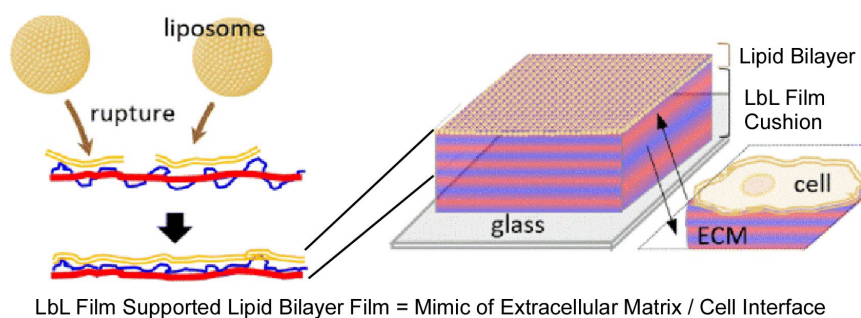
Figure 19. A lipid bilayer supported on a soft biopolymeric multilayer cushion to mimic the cellular interfacial environment, where a lipid bilayer mimicking a cell membrane was placed over a layer-by-layer (LbL) membrane cushion of polyelectrolytes composed of hyaluronic acid and poly-L-lysine. Reproduced under terms of the CC-BY license.[75] Copyright 2022, Anna Vikulina, Alena Wulf, Guy Guday, Rawil Fakhrullin, and Dmitry Volodkin, published by [Royal Society of Chemistry].

(Figure 19).[75] Specifically, a lipid bilayer mimicking a cell membrane was placed over a layer-by-layer (LbL) membrane cushion of polyelectrolytes composed of hyaluronic acid and poly-L-lysine. This study focuses specifically on the inward transport of polyelectrolytes through the lipid bilayer of model proteins, lysozyme and alpha-lactalbumin, into the multilayer membrane. The model membranes have several barrier properties in the transport of proteins. Electrostatic interactions between poly-L-lysine and externally added proteins govern the transport of proteins into the hybrid. Nanoarchitectonized lipid membrane/extracellular matrix structure-mimetic hybrids provide a very good venue for modeling a wide range of cell membranes, extracellular matrices, and related phenomena. This technically simple methodology opens new avenues for nanoarchitectonics at cell interfaces as extracellular matrix mimics.

Nanoarchitectonics of molecules that can recognize specific DNA sequences is also underway. Such synthetic ligands are promising for targeted disruption of transcription factor-DNA interactions. Tumor-sensitive signaling pathways can be controlled. Sugiyama, and co-workers reported on a sequence-specific cyclic pyrrole imidazole polyamide (Figure 20).[76] A cyclic pyrrole imidazole polyamide recognizing eight base pairs of DNA was synthesized. Cyclic pyrrole imidazole polyamides can target Gli-mediated transcription and inhibit the hedgehog pathway, which is thought to play a major role in cancer stem cell growth. Cancer stem cells are a small population of cells that reside within cancer tissue and play a major role in metastasis, drug resistance, and recurrence. Imaging evaluation of the penetration of cyclic pyrrole imidazole polyamides into
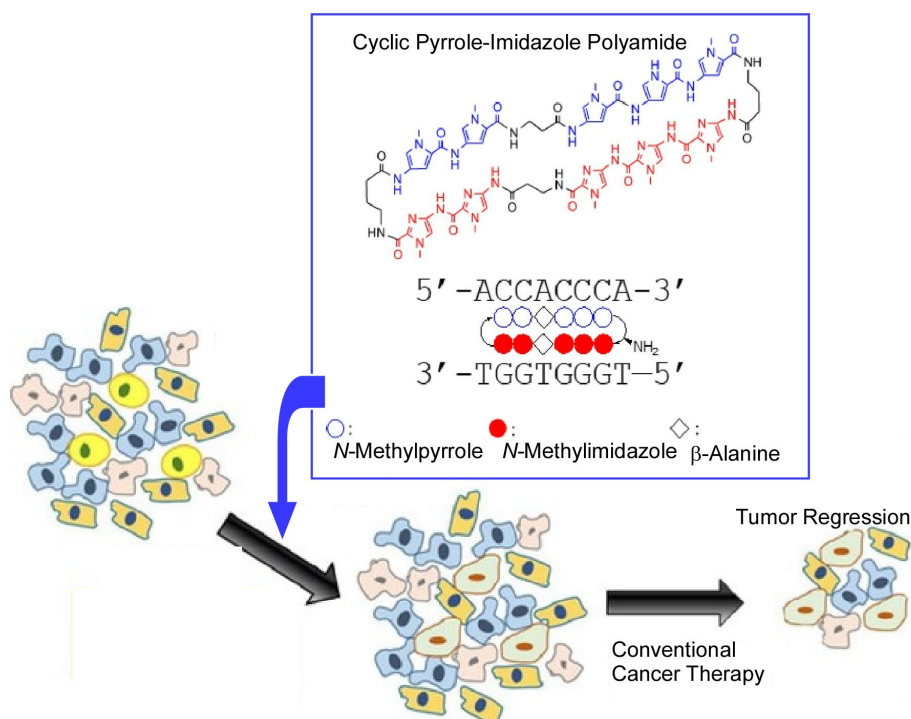

Figure 20. Control of Tumor-sensitive signaling pathways by synthesized cyclic pyrrole imidazole polyamide to recognize eight base pairs of DNA. Reproduced with permission.[76] Copyright 2022, Chemical Society of Japan.
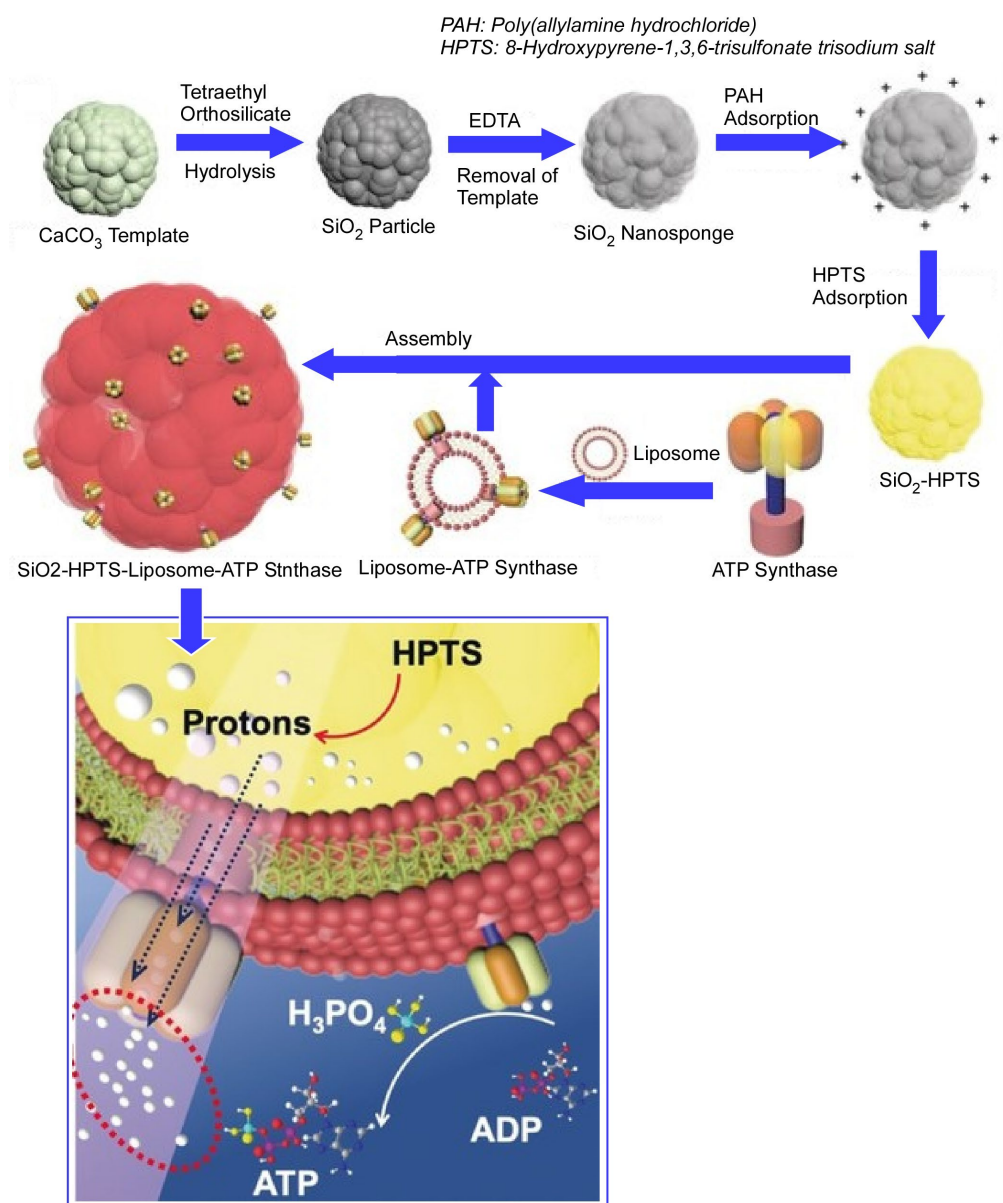
Figure 21. Hierarchical SiO2 nanosponges co-assembled with photoacid molecules and liposome-ATP synthase for achieving photophosphorylation output control to synthesize ATP upon light irradiation. Reproduced with permission.[77] Copyright 2018, Wiley-VCH.

eukaryotic cells showed that they localize to the nucleus. Cyclic pyrrole imidazole polyamide enhanced the cytotoxicity of temozolomide in glioma cell lines. When the combinatorial was evaluated in a leukemia cell line, it was found to enhance cytotoxicity along with RUNX inhibitors. It was also found to inhibit cell proliferation in brain tumor stem cells.

7. Cell-Mimic Nanoarchitectonics

In cells, various biomolecular machines and functional molecules are organized in the cell membrane to perform sophisticated functions. There, functional molecules are organized in a manner that is a model of nanoarchitectonics. Attempts are also being made to incorporate bio-highly functional molecules using objects such as liposomes and porous nanoparticles as matrices in place of cells. This is a nanoarchitectonics reproduction of cellular function.

Nanoarchitectonics of artificial biomimetic systems has the potential to achieve outputs that break the limits of natural reactions. Mimicking nature's unique structures and ingenious functions is a challenging task, but attempts to accomplish it have been reported. Li and coworkers have artificially integrated multiple biochemical reactions via molecular assemblies (Figure 21).[77] Inspired by the natural chloroplast compartment structure, they designed hierarchical SiO2 nanosponges. The nanosponges were co-assembled with photoacid molecules and liposome-ATP synthase to form organic-inorganic hybrid nanocomposites for achieving photophosphorylation output control. Upon light irradiation, protons are generated by photoacid generators in the confined space. As a result, the enzyme ATPase, encapsulated in liposomes, performs ATP synthesis. In other words, it can mimic the photophosphorylation process in vitro. Massive ATP production in vitro could be demonstrated. Furthermore, the photoswitch and pH jump trigger in a coupling system can be combined to demonstrate a sophisticated cascade reaction by
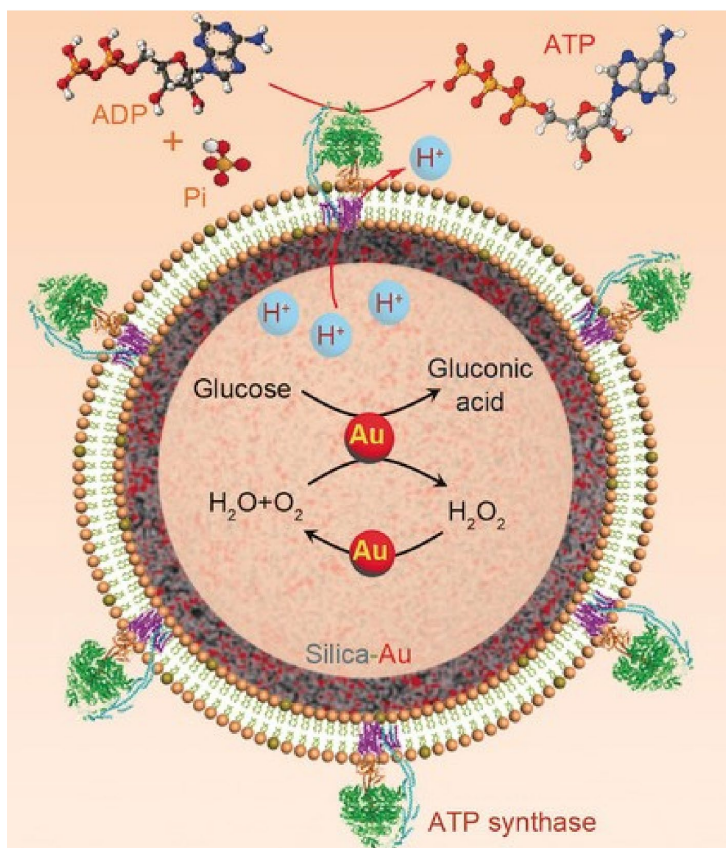
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Figure 22. Nanozyme-catalyzed cascade reaction with an oxidative phosphorylation function mimicking mitochondria with hollow silica microspheres containing trapped gold nanoparticles to catalyze cascade reaction and create proton gradient across the proteoliposome membrane, which promotes the synthesis of ATP by ATP synthase. Reproduced with permission.[78] Copyright 2019, Wiley-VCH.

molecular assembly. Following this methodology, bioinspired nanoreactors for photobiocatalysis can be fabricated. It also gives good design guidelines for new supramolecular assemblies to construct various biomimetic nanosystems.

A hybrid structure that performs a nanozyme-catalyzed cascade reaction with an oxidative phosphorylation function mimicking mitochondria was reported by Li and co-workers (Figure 22).[78] Hollow silica microspheres containing trapped gold nanoparticles were synthesized. The gold nanoparticles possess two enzyme-like activities corresponding to glucose oxidase and peroxidase. In the presence of oxygen, glucose is converted to gluconic acid by a gold nanoparticle-catalyzed cascade reaction. As a result, the ambient pH value decreases and a proton gradient is created. The protons then diffuse across the proteoliposome membrane coating on the surface of the hollow silica microspheres, which promotes the synthesis of ATP by ATP synthase. The hydrogen peroxide produced at the same time is consumed by the gold nanoparticles. The latter effect prevents oxidation of the ATP synthase. This nanoarchitectonized system exhibited high oxidative phosphorylation activity comparable to that of natural mitochondria. The natural-artificial hybrid prototype enables ATP production from bioenergy such as glucose. Application of this system will contribute to the development of biofunctions powered by ATP.

When nanoarchitectonics combines biofunctional molecules with artificial reactions, it is possible to create systems that perform bio-like functions while using chemicals that are different from those of living organisms. Those that mimic natural processes, leading to the production of biochemical fuels through oxidative and photosynthetic

phosphorylation, are shown above. Rather, Fei, Li, and co-workers have nanoarchitectonically created a system that uses boric acid as fuel and stores energy in a cell-like supramolecular structure (Figure 23).[79] In the developed system, the biomimetic supramolecular architecture uses polyelectrolyte microcapsules supporting ATP synthase-containing liposomes. In this system, the polyol forms cyclic boronates, which release protons from the boric acid. As a result, a controlled proton gradient across the lipid membrane is established. The incorporated ATP synthase is driven to produce the biochemical fuel ATP from adenosine diphosphate and inorganic phosphate. In total, boric acid is used as a chemical source to drive the ATP synthase. The rate of ATP production can be adjusted by polyol selection. Thus, a new route to achieve highly efficient bioenergy conversion can be developed. Such a nanoarchitectonics approach can extend the possibilities for synthesis and devices requiring biochemical fuels.

Nanoarchitectonics, which incorporates multiple biofunctional elements into an artificial system, has also been considered. Li, Dong, and workers and created cell-like microcapsules incorporating ATP synthase and bacteriorhodopsin to realize the interlocking function of these biofunctional elements (Figure 24).[80] In other words, by co-assembling bacteriorhodopsin and ATP synthase in an artificial biomimetic system, cascade reactions and ATP synthesis under illumination were enabled. Bacteriorhodopsin was oriented and immobilized by layer-by-layer (LbL) assembly with polyelectrolytes using MnCO3 microspheres as templates, which can be removed later. ATP synthase proteoliposomes were then coated onto the microcapsules by fusion. Upon light irradiation,
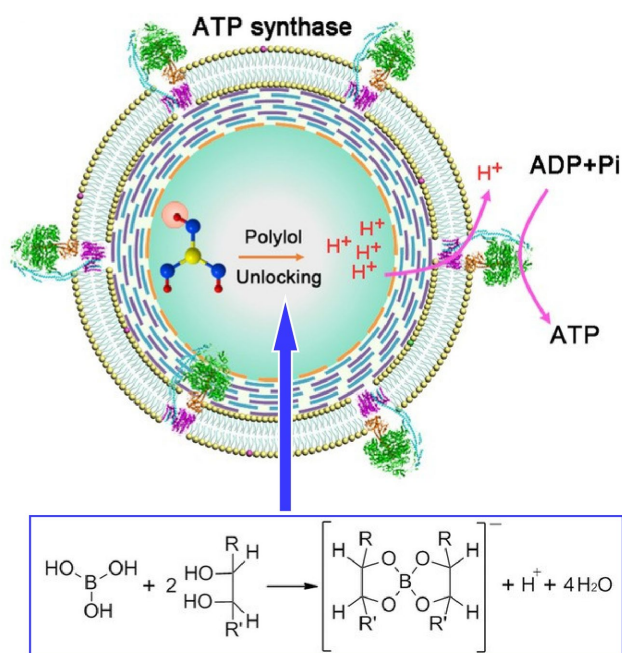
Figure 23. Biomimetic supramolecular architecture of polyelectrolyte microcapsules supporting ATP synthase-containing liposomes in which the polyol forms cyclic boronate to release protons and generate proton gradient across the lipid membrane for synthesis of ATP from adenosine diphosphate and inorganic phosphate by the immobilized ATP synthase. Reproduced with permission.[79] Copyright 2020, Wiley-VCH.
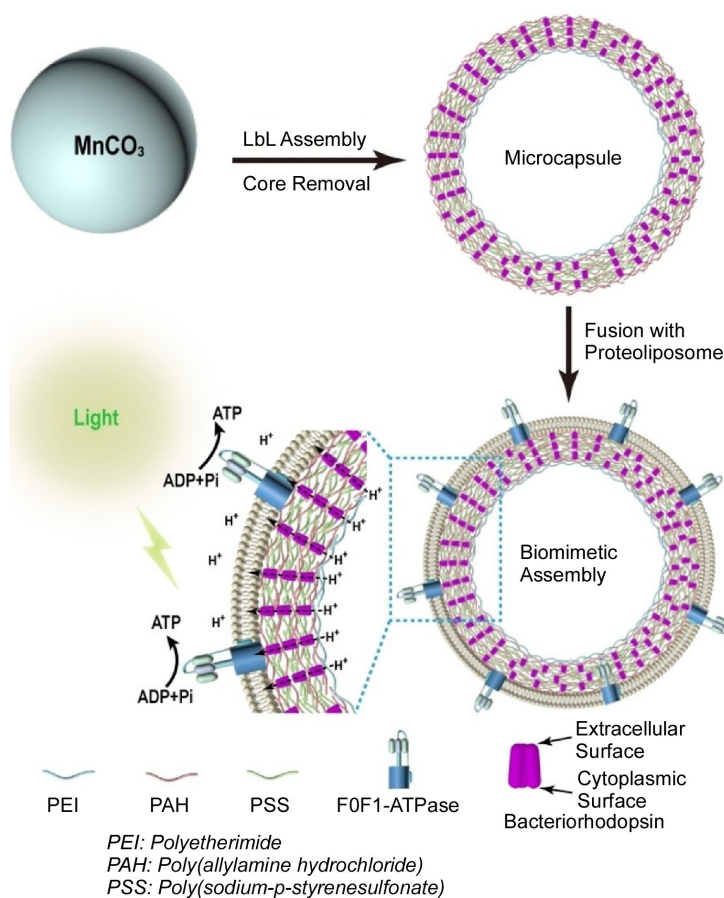
Figure 24. Cascade reactions and ATP synthesis under illumination by co-assembling bacteriorhodopsin and ATP synthase in an artificial biomimetic system of LbL assembly with polyelectrolytes using $MnCO_3$ microspheres as templates. Reproduced with permission.[80] Copyright 2022, Wiley-VCH.

the bacteriorhodopsin inside the microcapsule pumps protons from the inside to the outside. As a result, a proton gradient is formed throughout the proteoliposome. ATP synthase is activated and ATP is synthesized. In addition, the introduction of

Figure 25. Cell-in-Catalytic Shell upon Introducing a series of enzymes into a cytoprotective artificial shell on a living cell with enzymatic cascade reactions and exogenous reactions that are beneficial to the cells inside. Reproduced with permission.[83] Copyright 2022, Wiley-VCH.

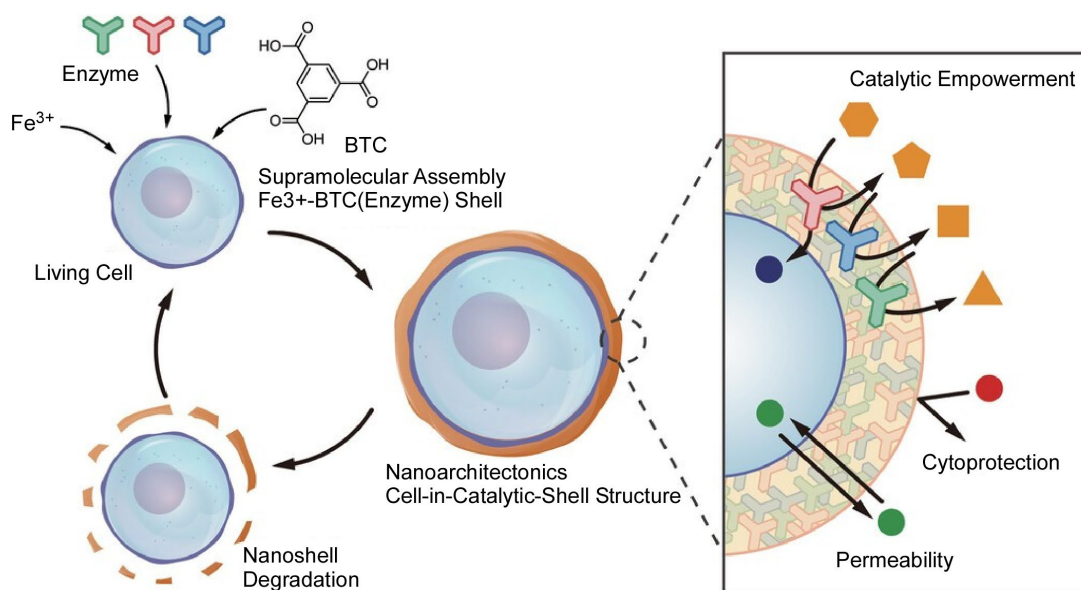quantum dots greatly enhances light-induced phosphorylation. Such a nanoarchitectonics design will open up new avenues for the utilization of light energy. In other words, a system can be constructed to increase the conversion efficiency of solar energy to ATP.

By performing nanoarchitectonics incorporating biomolecules with advanced functions, we can mimic artificially controlled biological functions. It is possible to couple an artificial reaction with ATP synthase or to coordinate the function of bacteriorhodopsin and ATP synthase. In doing so, liposomes and LbL capsules provide an ideal venue for organizing these biofunctional molecules. The nanoarchitectonically organized system is like a cell. In other words, cellular functions are reproduced by nanoarchitectonics.

8. Cell-Based Nanoarchitectonics

Beyond approaches that use nanoarchitectonics to mimic cellular function, some use the cell itself as a material for nanoarchitectonics. There are approaches that hybridize cells with artificial materials or artificially organize cells.

There is also nanoarchitectonics, which encapsulates living cells with artificial materials. For example, cyborg cells in which living cells are covered with LbL membranes have been proposed.[81] Hybrid structures in which living cells are covered with exogenous substances are also referred to as cell-in-shell biohybrid structures.[82] Of particular interest is the enhancement of the biological functions of cells through encapsulation and the introduction of entirely new functions. Choi and co-workers proposed in this report a method for introducing a series of enzymes into a cytoprotective artificial shell. This artificial shell can perform enzymatic cascade reactions and exogenous reactions that are beneficial to the cells inside (Figure 25).[83] Specifically, living cells were nano-encapsulated with supramolecular organometallic complexes of Fe^{3+} and benzene-1,3,5-tricarboxylic acid. A series of enzymes were embedded in situ in the shells without loss of catalytic activity. Confinement of the reaction intermediates in the internal voids of the nanoshells enhanced the catalytic efficiency of the multi-enzyme cascade reaction. Cells nano-encapsulated with enzyme-

containing shells acquired the ability to convert toxic chemicals into nutrients. For example, the ability to convert the lethal octyl-β-D-glucopyranoside to D-glucose has been conferred, and the cells have autonomous cytoprotective functions. Because the hydrophobic supramolecular organometallic complex layer effectively shuts out oily substances, nano-encapsulated cells are remarkably viable even under lethal conditions, such as in organic solvents. Such an approach contributes to the construction of cellular nanobionic systems. There is great potential in interfacing non-natural materials with living cells and in the biomedical and nanobiomedical fields. It can be a nanoarchitectonics method for engineering next generation cellular hybrid systems.

Covering the perimeter of a living cell with an artificial substance also provides a model for the extracellular matrix. This can be useful for clinical research. For example, high extracellular matrix stiffness is a prominent feature of malignant tumors. To elucidate the mechanistic link between increased matrix stiffness and tumor progression, it is necessary to develop an external chamber in which stiffness can be controlled. The matrix can be wirelessly and reversibly stiffened and softened multiple times and at different rates of change using an external magnet as reported by Tay and co-workers (Figure 26).[84] This structure was used to study the effects of dynamic matrix stiffness changes on three-dimensional cancer spheroids. An external static magnetic field was used to dynamically change the mechanical stiffness of the hydrogel to mimic healthy and malignant breast tissue. They found that matrix stiffness increased tumor malignancy, including denser cellular tissue, epithelial-mesenchymal transition, and hypoxia. An important finding was that softening the matrix could arrest or reverse malignant transformation. This mechanical rescue can enhance the drug effect due to the reduction of stress and downregulation of some cellular mechanotransducers. Such nanoarchitectonics systems provide a better understanding of the impact of matrix softening on cancer biology. It can be a powerful tool in applications such as drug screening in clinical trials.

Attempts are also being made to construct tissue-like structures in which cells are assembled. Such attempts are also
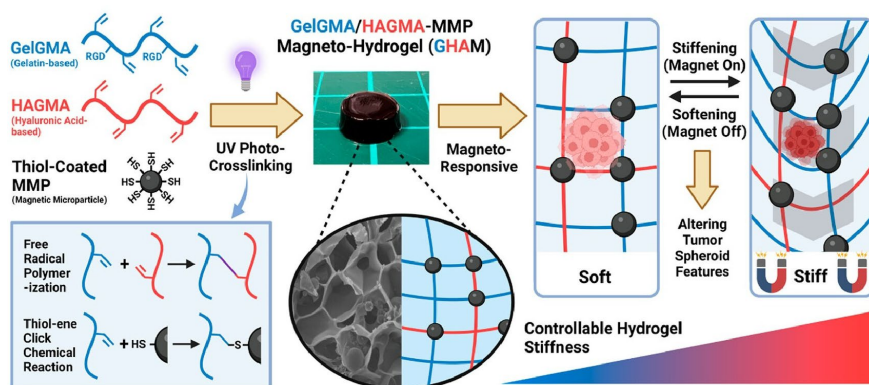
Figure 26. The matrix with capability of wirelessly and reversibly stiffening and softening using an external magnet to elucidate the mechanistic link between increased matrix stiffness and tumor progression. Reproduced with permission.[84] Copyright 2023, American Chemical Society.

attracting attention from other perspectives. The development of tissue-like structures such as cell sheets, spheroids, and organoids has contributed to the progress of regenerative medicine.[85] However, these artificial cellular tissue structures cannot provide sufficient oxygen to the interior of large tissues with high cell density. Therefore, it has been said that simultaneous achievement of scale-up and high cell density is difficult. Wu et al. fabricated in vitro blood vessels to supply oxygen to the interior of millimeter-sized scaffold-free tissues with a cell density of about 200 million cells/mL, comparable to native tissues.[86] A hierarchical vascular network with anastomosing capillaries and large blood vessels is essential for oxygen supply. The hierarchical vascular network was formed by a top-down approach. Human embryonic fibroblasts and human umbilical vein endothelial cells are co-cultured to produce cell sheets containing capillary networks. This sheet is used to create cell-dense tissue, and at the same time, artificial flow channels are formed in the tissue. Cell sheets containing capillaries are produced by co-culturing and then pressed into an epoxy resin mold to hold them in place to produce high cell density tissue. This method has been shown to form hierarchical vascular networks in cell-dense tissues in vitro. This could be a scaffold-free tissue technology in regenerative medicine with potential for scale-up. For example, it can be used for scale-up of organ buds produced from pluripotent stem cells.

In addition to atoms, molecules, supramolecules, nanomaterials, and biomolecules, the cell itself is a component of nanoarchitectonics. Hybridizing and organizing cells with artificial structures can create cellular systems that confer functions not available in the original cell. Such nanoarchitectonics can also create an artificial environment for studying cellular functions. In addition, nanoarchitectonics, such as cell organization, can contribute to fields such as regenerative medicine.

9. Short Perspectives

This review article has presented examples of nanoarchitectonics for a variety of objects. These are those that gather atoms, architect and assemble molecules, assemble inorganic nanomaterials, architect biomolecules into artificial tissues, use biological elements to constitute functional systems such as cells, and use cells themselves as architectural elements. From atoms and molecules, which are basic units, to living cells, which are complex systems, are all components of nanoarchitectonics. This paper does not exhaustively select all examples, but only those that are distinctive. Therefore, not all

of the scope is followed systematically. Even under such circumstances, the fabrication of functional materials and structures by nanoarchitectonics contributes to research in diverse fields. It also contributes to basic sciences such as the pursuit of molecular synthesis, the analysis of the assembling morphology of amphiphilic and fullerene molecules, and the control of the morphology of catalytic metals. On the other hand, there are also many other promising applications such as atom switches, high-entropy alloy catalysts, polyatomic quantum dots, non-stoichiometric control of doping, electronic and optical functions through anion mixing, organic synthesis via tip technology, nanorobots and microrobots, bioinspired nanomotors, high-performance carbon superstructures, highly active electrocatalysts for oxygen-evolving reactions, nanosheet chemical synthesis factory architecture, artificial biocatalysts, lipid membrane/extracellular matrix structure-mimicking hybrids, ATP production by artificial cells incorporating ATP synthase and bacteriorhodopsin, etc., cell-in-shell biohybrid structures, efficient photodynamic therapy of cancer cells, cancer stem cell suppression using artificial molecules, research on malignant tumor behavior using extracellular matrix models, and the creation of high cell density tissues using cell sheets containing capillaries. The examples of potential contributions to a variety of advanced fields.

Instead of using ready-made materials, diverse functions can be created by building from various elements. This is made possible through nanotechnology by learning the secrets of the nano and introducing them into various basic material sciences. This is what nanoarchitectonics brings about. Ideally, this concept would be complete if we could architect functional materials universally from atoms and molecules. That is not easy. The molecules that make up the unit are diverse and the target functions are infinite. It may be impossible to address this through conventional scientific systematization. Fortunately, mankind is developing new fields, such as materials informatics[87] and machine learning,[88] which incorporates artificial intelligence (AI) technology into materials science to determine how to synthesize materials. It is anticipated that incorporating these methods into nanoarchitectonics will be significant. Methodologies that incorporate a large number of elements and their functional possibilities could be developed using both the concept of nanoarchitectonics and AI technology.[89] In this way, a method for everything on materials science to develop functional molecules universally may be completed. This becomes the fundamental global challenge in materials science. On the other hand, imaging future mass

productions of these materials created by nanoarchitectonics, some factors such as cost and scalability are also necessary challenges for practical application.

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Graphical Abstract

Nanoarchitectonics: Method for Everything in Material Science

Katsuhiko Ariga

<Summary>
Nanoarchitectonics is supposed to build functional materials using atoms, molecules, and nanomaterials as building blocks. All materials are made of atoms and molecules. Thus, nanoarchitectonics can be a universal way to create all materials. It may be said to be the method for everything in material science. This becomes the fundamental challenge in materials science.

<Diagram>