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RESPONSIVE MATERIALS Open Access WILEY

REVIEW ARTICLE

Responsive materials nanoarchitectonics at interfaces

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Abstract

Advanced materials could perform functions in response to external stimuli. These are responsive materials. In order for us to develop advanced functional systems with a good responsive nature, we need to create a methodology that goes one step further. It is the artificial architecture of functional material systems based on the knowledge of nanotechnology. The task will be fulfilled by the new concept of nanoarchitectonics. Nanoarchitectonics integrates nanotechnology with various material sciences, basic chemistry, microfabrication techniques, and biological processes to architect functional material systems from atomic, molecular, and nanomaterial units. This review will deal with the nanoarchitectonics of responsive materials related with phenomena at interfaces. In order to demonstrate the effectiveness of responsive materials nanoarchitectonics at interfaces for functional systems of various sizes, this review article is organized by size for various functional systems. Specifically, this review has grouped them into (i) molecular level response, (ii) nanodevice level response, (iii) material level response, and (iv) living cell level response. If the social demand for these materials is fully recognized, such development is expected to efficiently progress. This review article would play a role in stimulating such development.

Keywords
interface, living cell, nanoarchitectonics, nanodevice, responsive materials

1 | INTRODUCTION

The development of humankind is heavily dependent on the development of materials. Since time immemorial, mankind has extracted materials from nature and used them. Subsequent developments in various sciences have made it possible to create materials that perform desired functions. Many early materials were used to form structures or for simple tasks. However, more advanced materials began to be created that could perform functions in response to external stimuli. These are responsive materials.[1–5] Various materials have been shown to function as responsive materials with various purposes including sensing,[6–8] energy,[9–11] environment,[12–14] device,[15–17] and biomedical applications.[18–20] In the process, it has become clear that it is not the material itself, but the precision of its precise structure that leads to more advanced functions.

A major factor that has paved the way for such a path is initiation of nanotechnology. Nanotechnology has made it possible to observe and manipulate structures at the atomic, molecular, and nano-level.[21–23] It has also made it possible to characterize nano-level properties.[24–26] As a result, it has become clear that there are unique phenomena such as quantum effects at the nanoscale that are different from macroscopic phenomena.[27,28] It has been found that materials exhibiting superior functionality have rational structures at the nano-level.[29,30] In particular, the structure of functional systems in the biological world has been found to be a superb organization of molecular units, exhibiting highly characteristic and highly efficient functions. In biological functional systems, functional molecules often line up to flow or accumulate information, energy, and electrons in specific directions in response to external stimuli. For example, photosynthesis[31] and signal transduction[32] can be regarded as extremely well designed responsive materials.

In order for us to develop advanced functional systems like those found in living organisms, we need to create a methodology that goes one step further. It is the artificial architecture of functional material systems based on the knowledge of nanotechnology. The task will be fulfilled by the new concept of nanoarchitectonics (Figure 1).[33,34] While nanotechnology was originated by Richard Feynman in the middle of the 20th century,[35,36] nanoarchitectonics was proposed by Masakazu Aono in the beginning of the 21st century.[37] Nanoarchitectonics can be considered a post-nanotechnology concept.[38]

Rather than an entirely new concept, nanoarchitectonics combines existing research fields. Nanoarchitectonics integrates nanotechnology with various material sciences, basic chemistry, microfabrication techniques, and biological processes to architect functional material systems from atomic, molecular, and nanomaterial units.[39,40] Materials construction by nanoarchitectonics strategy includes atomic and molecular manipulation, physical and chemical conversion, self-assembly and self-organization, orientation and organization by external fields, nano- and micro-level fabrication, biochemical and biological processes, which are selected and combined during the nanoarchitectonics processes.[41–43] This methodology is independent of the substance and its application. It is used to construct a variety of functional systems using a variety of substances including materials synthesis,[44–46] structure fabrication,[47–49] basic physics,[50–52] catalysis,[53–55] sensors,[56–58] devices,[59–61] energy,[62–64] environmental,[65–67] biochemistry,[68–70] and biomedical issues.[71–73] Originally, materials are composed of atoms and molecules. Therefore, the concept of nanoarchitectonics can be considered to lead to the creation of all matter. It is considered to be regarded as the method for everything in materials science,[74,75] which corresponds to the theory of everything in physics.[76]

The creation possibilities of responsive materials by nanoarchitectonics would expand to a very large area. Therefore, it is impossible to discuss all of them here. Therefore, this review will deal with the nanoarchitectonics of responsive materials related with phenomena at interfaces. At solid interfaces, atoms and molecules can be precisely observed and evaluated.[77,78] At liquid interfaces, molecules and materials can move and accumulate.[79,80] In some aspects, it is easier to approach the consideration of a material system trapped in a two-dimensional system than to examine a material system spread out in three-dimensional space. In order to demonstrate the effectiveness of responsive materials nanoarchitectonics (MANA) at interfaces for functional systems of various sizes, the following sections are organized by size for various functional systems. Specifically, this review has grouped them into (i) molecular level response, (ii) nanodevice level response, (iii) material level response, and (iv) living cell level response. The examples discussed are not necessarily the most advanced or representative of the fields. Some typical examples are discussed to show that they can be applied from the atomic/molecular level to the living cell level.

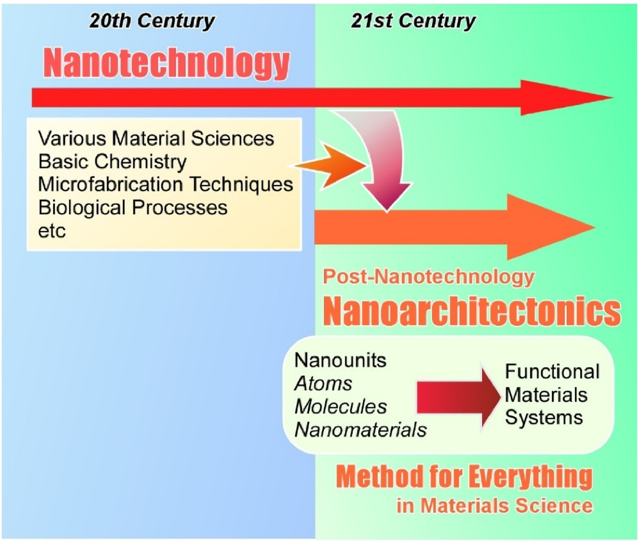

FIGURE 1 Outline of nanoarchitectonics concept.

2 | MOLECULAR LEVEL RESPONSE

Consider building a stimulus-response system at the smallest level of structure. This would be a molecular machine in which each molecule moves like a machine in response to stimuli.[81–83] However, in the early days of molecular machine research, the behavior of a molecular machine dissolved in solution was mainly evaluated as the sum of its huge molecules. Later, with the advancement of nanotechnology, it became possible to actually observe and evaluate the movement of molecular machines. Successful examples of this realization are the development of nanocars[84,85] and nanocar race.[86,87] From the viewpoint of nanoarchitectonics, it is significant to examine a system in which several molecules work together, rather than the movement of a single molecule.

One such example was reported by Moresco and coworkers who demonstrated collective rotational transmission between three molecular gears.[88] Thus, the transmission of rotation along a row of molecular gears is an essential element in the construction of molecular mechanical machines. First, an important condition is that the molecular gears must move stably. In order to stably drive the molecular gear train at the tip of a scanning tunneling microscope (STM), each gear molecule must be stably anchored to a metal surface. The anchoring required for immobilization is facilitated by the radical state of the molecules induced by dissociation reactions. That such an open radical state in the nucleus of star-shaped pentaphenylcyclopentadiene is favorable for anchoring was also demonstrated by density functional theory calculations. To enable the transmission of motion by STM manipulation, the molecular gear requires a functional group to ensure interaction with the tip. In the reported system, it was found to be effective to place a *tert*-butyl group on one tooth end of the gear. The presence of a *tert*-butyl group is not only advantageous for molecular manipulation by the tip, but also for monitoring gear rotation. By manipulating it as a screwdriver, a step was created in the rotational transmission between the three meshing gears (Figure 2). When rotated counterclockwise from the driver (green), follower 1 (blue) rotated clockwise, while follower 2 (yellow) rotated counterclockwise at the same time. The series of behaviors and their observation require a very specific energy pathway on the ground state potential energy surface. Furthermore, the effects are interdependent. The steric *tert*-butyl tag is advantageous for manipulation by the tip and stabilizes the gear. At the same time, however, it prevents further transmission of rotation. For the development of molecular mechanical machines such as mechanical calculators, the controllability of the rotation of a large number of gears in a train is particularly important.

The electron beam can also be used as a stimulus to induce chemical reactions in molecules, which can then be precisely observed. Lungerich and coworkers demonstrated that electron beams can be used for synthesis.[89] The formation of double-hole fullerene-porphyrin cage structures from benzoporphyrin precursors deposited on graphene was observed and studied in detail using single molecule, atomic resolution, time-resolved transmission electron microscopy (Figure 3). The ability of the hybrid to host up to two lead atoms was demonstrated through real-time imaging analysis. The dynamics of the lead-lead bonding motif in this exotic organometallic cage structure was also analyzed and subsequently examined. After discussion, including a simulation study, it was concluded that the secondary electrons that accumulate around the irradiated region may also be responsible for the chemical reaction. This means that not only the fast primary electrons, but also the much slower secondary electrons in the beam shadow must be taken into account in the chemical transformation. Although understanding of fast electron-induced molecular reactions is still in its infancy, cinematic observations such as these can reveal a great deal. Single-molecule atomic-resolution time-resolved electron microscopy is a powerful tool for this purpose. It will also provide information on the kind of synthetic reactions that can be expected from focused electron beam-induced reactions. In addition, understanding radiation chemistry at the molecular level will have a profound impact on the design and fabrication of well-defined topological nanostructures using electron beam lithography techniques. It will also make a significant contribution to nanoarchitectonics at the molecular level.

In terms of the induction of organic reactions by external stimuli and detailed observation, reactions can be controlled by stimuli such as the application of local voltage from the tip of a probe microscope. This is also called local probe chemistry.[90,91] Kawai, Kubo, Foster, and co-workers have combined low-temperature scanning tunneling microscopy with density functional theory calculations to study dehydroazulene units in three-dimensional organometallic compounds on Ag(111).[92] Target compounds on Ag(111) using a combination of low-temperature scanning tunneling microscopy and density functional theory calculations. In this system, a reversible chiral switch of dehydroazulene units is induced by the application of a local probe-induced structural isomerization large bias voltage. The application of a tip-induced voltage pulse results in the formation of diradical species by successive homolysis of the two C-Br bonds of the naphthyl group (Figure 4). It is then converted to the chiral dehydroazulene moiety. The delicate balance of the reaction rate between the diradical and the two stereoisomers can be controlled by the in-line arrangement of the tip and molecular unit. The result is a controlled local probe structural isomerization of the azulene to azulene and azulene to diradical. The diradical moiety hosts an open-shell singlet that can undergo an inelastic spin transition from antiferromagnetic to ferromagnetic. Theoretical calculations suggest that the singlet undergoes an inelastic spin transition to a ferromagnetically coupled triplet state. Calculations of the energy barrier to isomerization also prove that isomerization does not occur at low temperatures without the influence of the tip. The high degree of chiral control of the dehydroazulene sequence by tip-induced isomerization was also demonstrated. Molecular nanoarchitectonics with such detailed structural observations provides a means by which the structure of units of molecular arrays can be rationally controlled. The structural control of such localized molecular arrays and the analysis of their functional properties will greatly contribute to the development of molecular optical, electronic, and magnetic devices

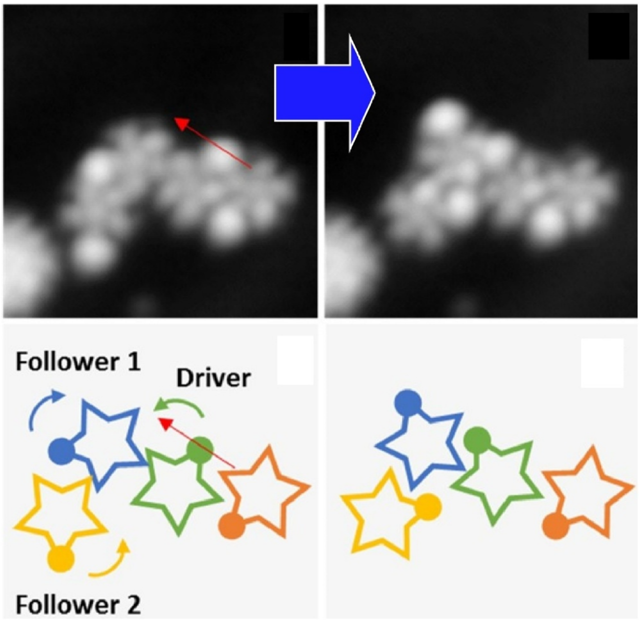

FIGURE 2 Rotational transmission between the meshing gears in which the driver (green) rotated counterclockwise, follower 1 (blue) rotated clockwise, while follower 2 (yellow) rotated counterclockwise at the same time. Reproduced with permission.[88] 2020, American Chemical Society.

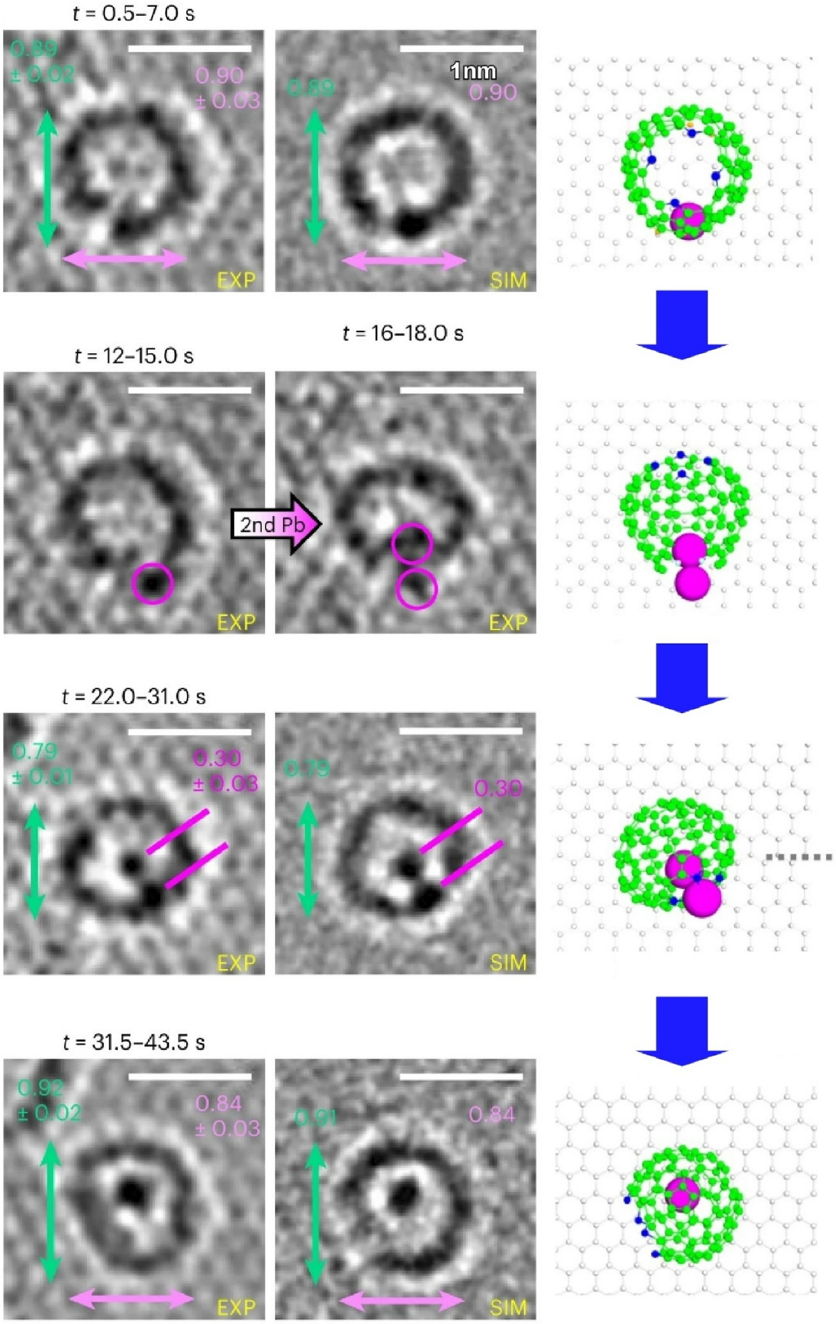

FIGURE 3 The double-hole fullerene-porphyrin cage structures with ability of the hybrid to host up to two lead atoms observed using single molecule, atomic resolution, time-resolved transmission electron microscopy. Reproduced with permission.[89] 2023, Springer-Nature.

based on localized molecular array structures. In addition, tip-based vertical systematic isomerization is important for advances in nanochemistry and molecular nanoarchitectonics, where molecular systems are fabricated molecule by molecule.

The stimulus of atomic manipulation by the tip of a probe microscope can control the physical properties of nanomaterials. For example, the control of magnetic topological states by spin polarization in extended π-carbon systems has great potential for spintronics applications. Foster, Kawai, and co-workers used low-temperature scanning tunneling microscopy to observe and manipulate the spin polarization in real space in a heteroatom-substituted system.[93] Because Si atoms are strongly bound to the B site, resulting in large corrugation amplitudes, their atomic manipulation can cause significant changes in the electronic properties of boron-substituted graphene nanoribbons. Therefore, they attempted to remove Si atoms by vertical manipulation with a tip

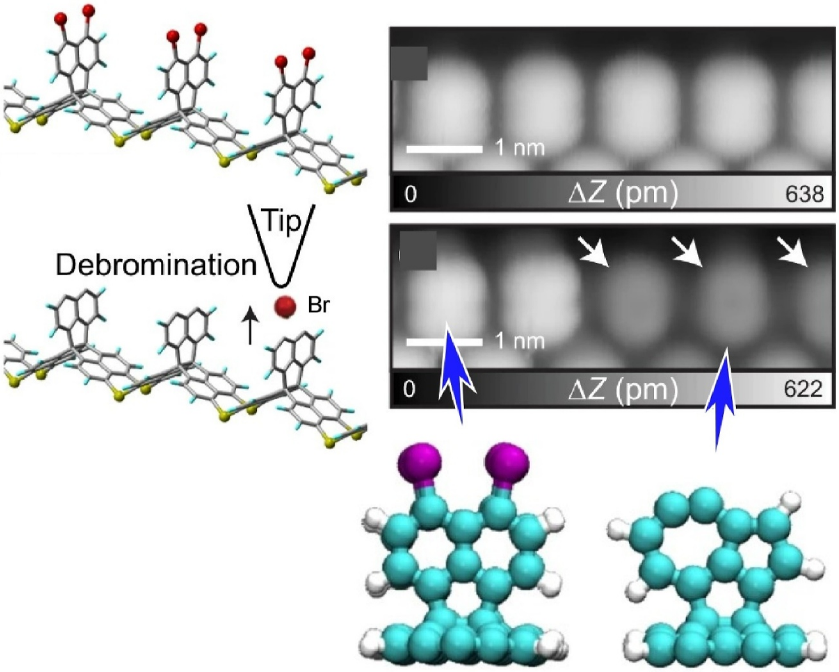

FIGURE 4 Formation of diradical species by successive homolysis of the two C-Br bonds of the naphthyl group though the application of a tip-induced voltage pulse. Reproduced under terms of the CC-BY license.[92] 2023, Springer-Nature.

(Figure 5). First, after positioning the tip at the Si site, the Z feedback of the tunnel junction was deactivated. Then, the tip was moved close enough to obtain a single-atom conductance gap and then retracted. After removal of Si atoms, a brick-like contrast appeared around the boron sites in the STM topography. This image was very different from boron-substituted graphene nanoribbons formed directly on Au(111) or on AuSiX layers without adsorbed Si atoms. A clear Kondo resonance peak appeared, which was further split by applying a 12 T magnetic field. This magnetic state can be relayed along the longitudinal axis of the graphene nanoribbon by sequential removal of Si atoms. In other words, this manipulation process can be repeated while effectively moving spin sites along the longitudinal axis of boron-substituted graphene nanoribbon. The result is local-probe spin engineering. This demonstration may point the way to the control of spin states in quantum materials.

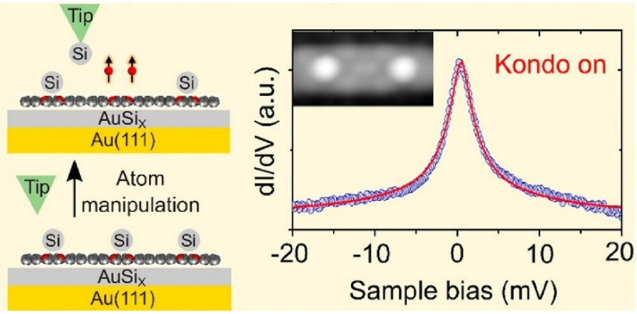

FIGURE 5 Removal of Si atoms by vertical manipulation with a tip form boron-substituted graphene nanoribbons formed directly on Au(111)/AuSiX layers resulting in clear Kondo resonance peak. Reproduced with permission.[93] 2022, American Chemical Society.

3 | NANODEVICE LEVEL RESPONSE

Various devices consist of a mechanism in which the response such as the current flowing in a circuit changes in response to a signal. Molecular switches, in which molecules play the role of the switch part, continue to be studied as ideal systems for ultra-small devices.[94,95] The switch part of the circuit, in which clusters of atoms are formed, is being studied as an atomic switch.[96,97] In any case, attempts are being made to develop stimulus-responsive devices through atomic and molecular nanoarchitectonics. Typical examples are given below.

Tsuruoka and co-workers investigated resistance change memory using silver ion-conducting solid polymer electrolytes.[98] This is the first report of an electrochemical atomic switch realized using organic materials. A simple Ag/solid-state polyelectrolyte/Pt structure containing a polyethylene oxide-silver perchlorate complex exhibited bipolar resistance switching under bias voltage sweep (Figure 6). The behavior was analyzed by electrical conductivity, glass transition temperature, transport number, and cyclic voltammetry measurements. The results show that the observed switching behavior is the result of the formation and dissolution of Ag

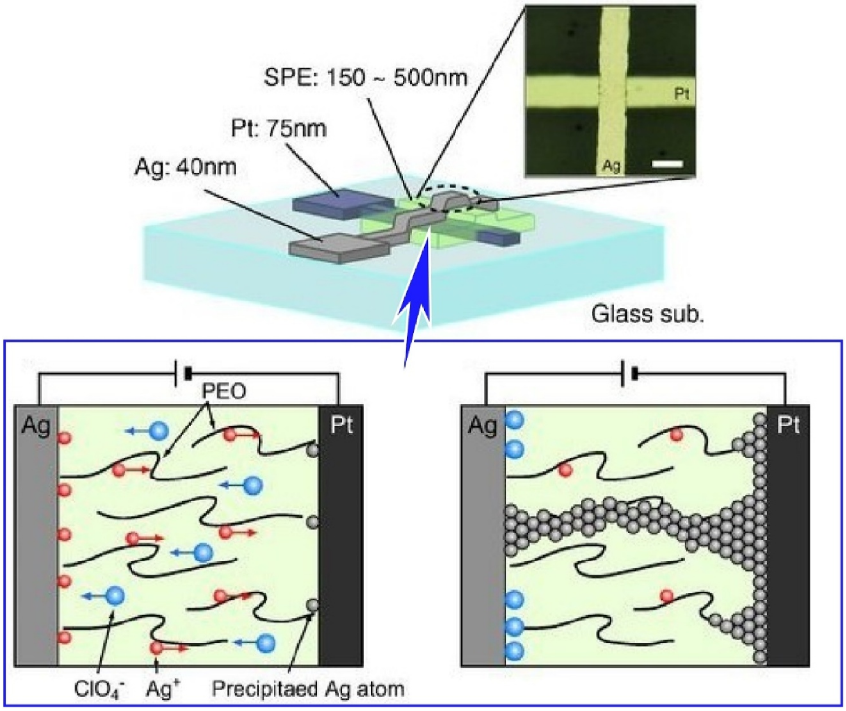

FIGURE 6 An electrochemical atomic switch with Ag/solid-state polyelectrolyte/Pt structure containing a polyethylene oxide-silver perchlorate complex where a metal filament can be formed between the two electrodes. Reproduced with permission.[98] 2010, Wiley-VCH.

metal filaments in the polymer electrolyte membrane by electrochemical reactions. When a positive bias is applied to the Ag electrode in the first sweep cycle, the Ag^+ and ClO_4^- ions in the electrolyte membrane move toward the Pt and Ag electrodes, respectively. In addition, some of the Ag atoms at the Ag-electrolyte interface are oxidized to Ag^+ ions by the anodic dissolution reaction $Ag \rightarrow Ag^+ + e^-$. Ag nuclei then grow preferentially toward the opposite electrode. Eventually, a metal filament is formed between the two electrodes. This filament formation leads to a low-resistance (ON) state of the cell. At this point, it is inferred that the thinnest part of the metal filament is only a few nanometers in diameter, as the cell exhibits an ON resistance on the order of kΩ. The device exhibits an ON/OFF resistance ratio in excess of 10^5. It also exhibits a programming speed in excess of 1 μs and a retention time in excess of 1 week. Such polymer electrolyte-based electrochemical devices are expected to be particularly suitable for flexible switch and memory applications.

Mallik, Tsuruoka, Nayak, and co-workers studied triptycene azo-polymers as switch materials for atomic switches (Figure 7).[99] The noncompliant structure of the triptycene motif in polymers causes inefficient packing of the polymer chain. This results in microporosity in the polymer matrix, which is favorable for metal filament development. The resistive switching properties of triptycene azo-polymers were investigated by current-voltage measurements based on current atomic force microscopy. In particular, volatile and nonvolatile switching was demonstrated depending on the amplitude of the bias voltage and the sweep cycle. Repeated voltage sweeps with varying voltage application interval time resulted in a transition in switching behavior from volatile to nonvolatile. In other words, repeated voltage sweeps lead to a short-term memory to long-term memory transition. This behavior is supposed to mimic the learning process of the human brain. The low-resistance state is found to result from the quantization of conductance by an integer factor of a single atomic point contact in the Ag filament formed between the current atomic force microscope tip and the Ag electrode. The switching time from the high-resistance state to the low-resistance state decreases exponentially as the amplitude of the voltage pulse increases. This suggests that the nucleation of metal atoms is likely a rate-limiting process. These results indicate that atomic switches based on triptycene azo polymers have great potential for organic neuromorphic electronics.

Field-mediated neurotransmission due solely to extracellular field effects has been postulated in biological synaptic systems. Mimicking this, Mishra, Nayak, and co-workers demonstrated field-mediated signal transduction to low-bias stimuli using an Ag_2S gap-type atomic switch (Figure 8).[100] In other words, they demonstrated ephaptic transmission solely by electric field effects in an AgS-gap atomic switch. The gap structure, which mimics a synaptic gap, is realized by placing a Pt-coated atomic force microscope tip on the AgS thin film with controlled contact forces. The hysteresis increase corresponding to input energies from

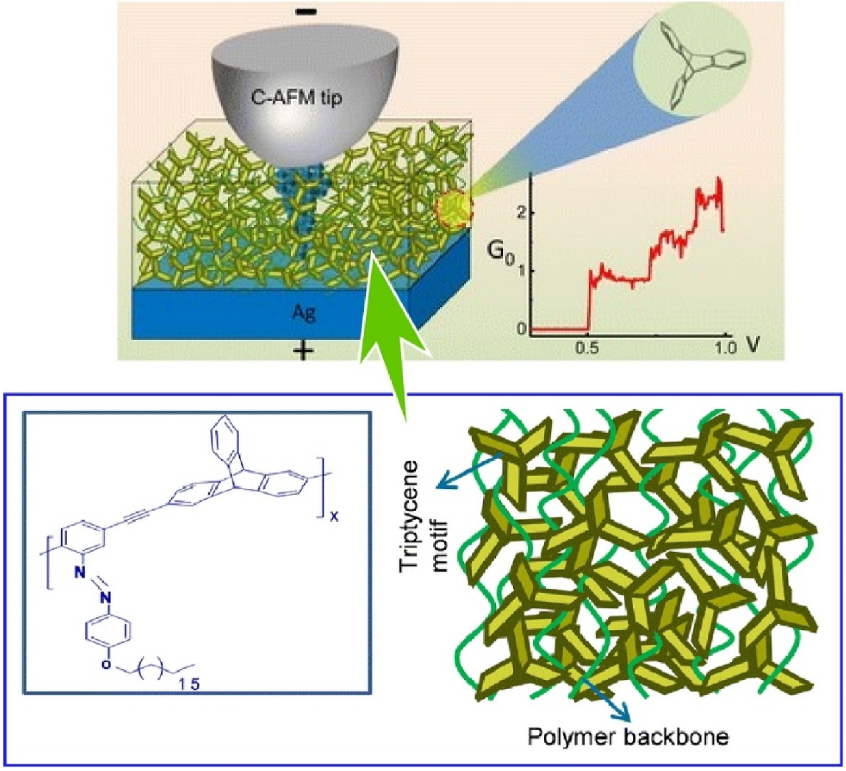

FIGURE 7 An atomic switch with triptycene azo-polymers as switching media with favorable development of metal filament development upon inefficient packing of the polymer chain. Reproduced with permission.[99] 2022, Royal Society of Chemistry.

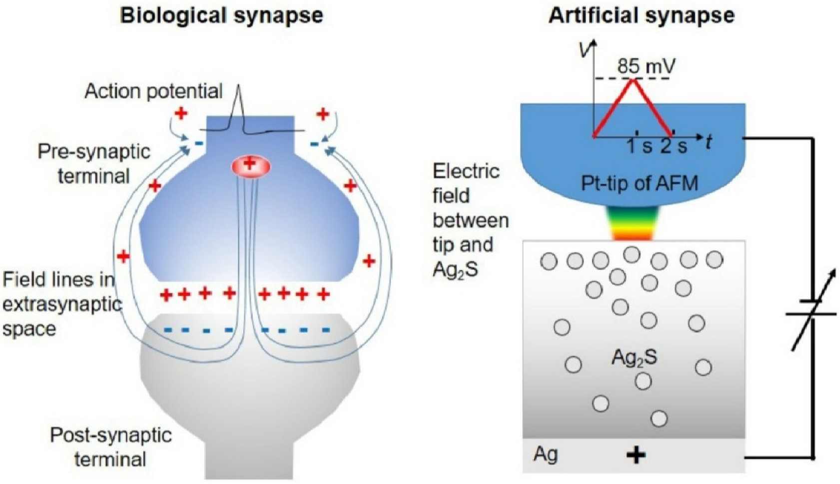

FIGURE 8 Field-mediated neurotransmission due solely to extracellular field in biological synaptic systems (left) and field-mediated signal transduction to low-bias stimuli using an Ag_2S gap-type atomic switch (right). Reproduced with permission.[100] 2024, Elsevier.

10 to 1000 pJ was observed. Signal transduction at biological synapses can occur when local electric fields generated at presynaptic terminals induce depolarization and hyperpolarization of postsynaptic terminals. Although not strong enough to mediate synaptic activation, they can affect neighboring cells and create waves of activation throughout the network. Similarly, at an atomically switched synapse, the subthreshold potential before electrochemical precipitation causes current flow solely due to field effects through the high-resistance tunnel gap. In systems under weak activation, the current is

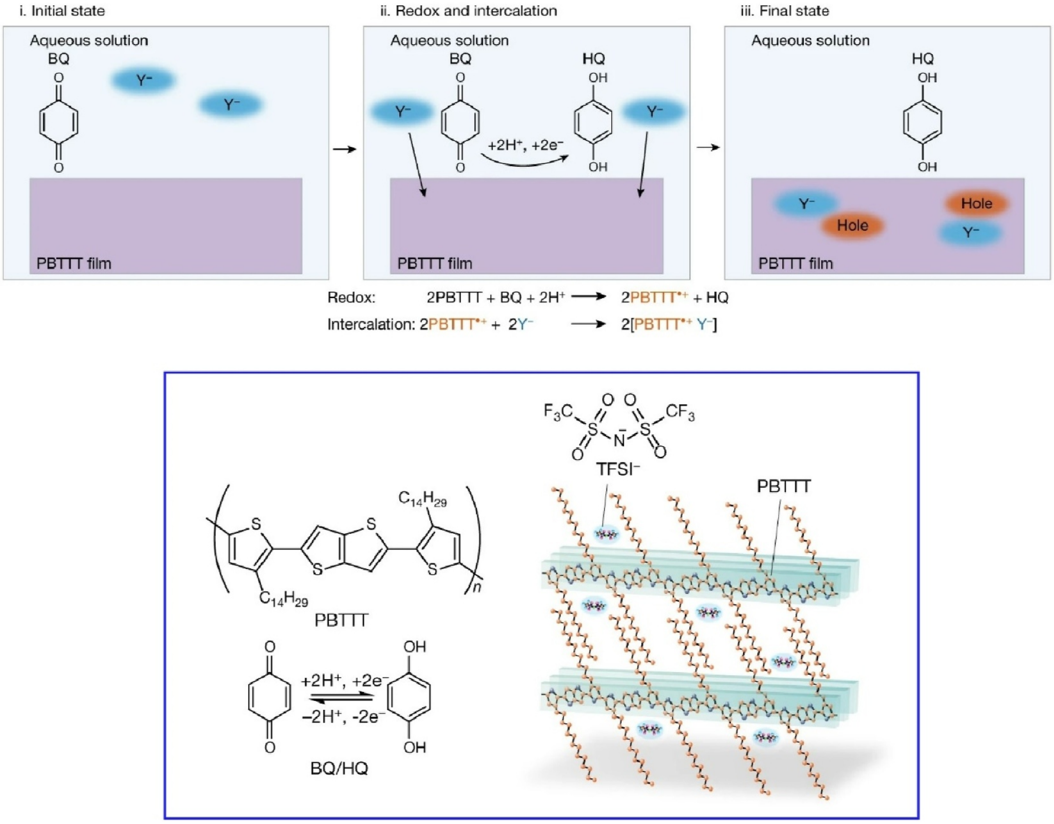

FIGURE 9 Chemical doping of crystalline organic semiconductor thin film upon the synergistic reaction of proton coupled electron transfer reaction and ion intercalation using the redox pair of the proton coupled electron transfer reaction and hydrophobic molecular ions. Reproduced with permission.[101] 2023, Springer-Nature.

small, but indicates that there is communication between the two terminals that has the potential to modulate the next signal response. This can modulate the spike timing activity of the neural network by synchronizing spatially distant sites. This is the basic synaptic behavior for all neurotransmission. The complex transmissions and interactions that occur in the synaptic cleft design the memory patterns of the human brain and create perceptions unique to each individual. This system is an important exemplar for the development of artificial neural networks that can mimic the communication via electric fields found in the cerebellum, heart, retina, and olfactory system.

Thin films of organic semiconductors and other materials are also used to carry the electrical properties of device functions. Ishii, Yamashita, and co-workers focused on proton-coupled electron transfer reactions,[101] which are widely used in biochemical processes, and developed a chemical doping process controlled by an unconventional parameter called proton activity (Figure 9). First, a p-type organic semiconductor thin film was immersed in an aqueous solution containing the redox pair of the proton coupled electron transfer reaction and hydrophobic molecular ions. Here, a benzoquinone/hydroquinone pair was used for the two-electron two-proton proton coupled electron transfer reaction. The synergistic reaction of proton coupled electron transfer reaction and ion intercalation resulted in efficient chemical doping of crystalline organic semiconductor thin films under room temperature conditions. According to the Nernst equation, the redox potential of the redox pair and the Fermi level of the organic semiconductor thin film were reproducibly tuned with high accuracy depending on the pH of the doping solution. This method has significant advantages in its ease and versatility over conventional chemical doping methods, which are performed in aqueous solution under standby and in an inert atmosphere in vacuum or in organic solvents. In other words, it has superior controllability, stability, and scalability. The ease of solution processing makes this method applicable to a wide variety of structures. This doping nanoarchitectonics is expected to contribute significantly to the fabrication of advanced and reliable organic semiconductor-based devices and bioelectronics, including sensors. The concept of this method will also link semiconductor doping with any chemical or biochemical process that can alter proton activity. It could thereby serve as a platform for environmental semiconductor processes and biomolecular electronics.

The structure of a few molecular layers can be created by crystallization of organic semiconductors. Transistor devices with gate structures on both sides can be created. Kumagai, Kasuya, Takeya, and co-workers have created solid and ionic gel gate dielectrics on the bottom and top surfaces, respectively, of bimolecular-thick single crystals of p-type organic thin-film transistors (Figure 10).[102] The charge transport properties at individual interfaces between the morphologically compatible organic thin-film transistor surfaces and different gate dielectrics were investigated. The results reveal the important influence of the gate dielectric material on the interfacial charge transport. Gate bias was applied through both dielectrics. In other words, a solid-state/ion-gel dual-gate transistor was operated. In this case, the hole mobility at the solid gate interface was 1.5 times higher. It is thought that the electric double layer formed on the ion-gel/homogeneous crystal surface provided a near-ideal charge transport interface due to dramatic trap filling. Thus, this dual-gate organic thin-film transistor geometry may be suitable for studying the inherent charge-carrier mobility of various organic semiconductors with high ionization potentials and large organic thin-film transistor threshold voltages.

4 | MATERIAL LEVEL RESPONSE

Nanoarchitectonics of diverse components is useful not only for phenomena at the atomic and molecular level, but also for the construction of stimulus-response systems at the material level. For example, controlling material orientation and properties through light stimulation is a common practice. In a recent review, Seki summarized the photoinduced structural control of azobenzene derivatives and azobenzene polymers with nanoarchitectonics on their surfaces.[103] Azobenzene is a simple rod-shaped photochromic molecule that has been widely studied. Nevertheless, new applications of photoswitching molecules and polymer systems are still being actively proposed. In particular, many attractive new kinetic functions have been realized by linking azobenzene molecules to liquid crystals and polymer systems. These useful functions are manifested by nanoarchitectonics at the interface. Azobenzene-containing monolayers and liquid crystalline polymer films created at the interface can be endowed with a variety of functions. Surface photo-orientation of liquid crystals, photoorientation of hierarchical structures, photodynamic motion and morphological switching in block copolymer monolayers, high-density brush and photo-triggered mass transfer of azobenzene side chain liquid crystal polymers, and polymer motion by Marangoni flow are examples. Stimulation of matter by light has the advantage of generating several types of information at once in a non-contact manner. When light is irradiated to a photoreactive molecular layer or polymer film layer with linearly polarized light or oblique irradiation, angle-selective photoreactions occur in the in-plane direction. Especially when liquid crystal materials are used, strong molecular cooperativity leads to obvious molecular orientation and provides a large orientation order. Such diverse methodologies can be applied to other photochromic molecules and polymers. It will be a useful tool for photo-stimuli-

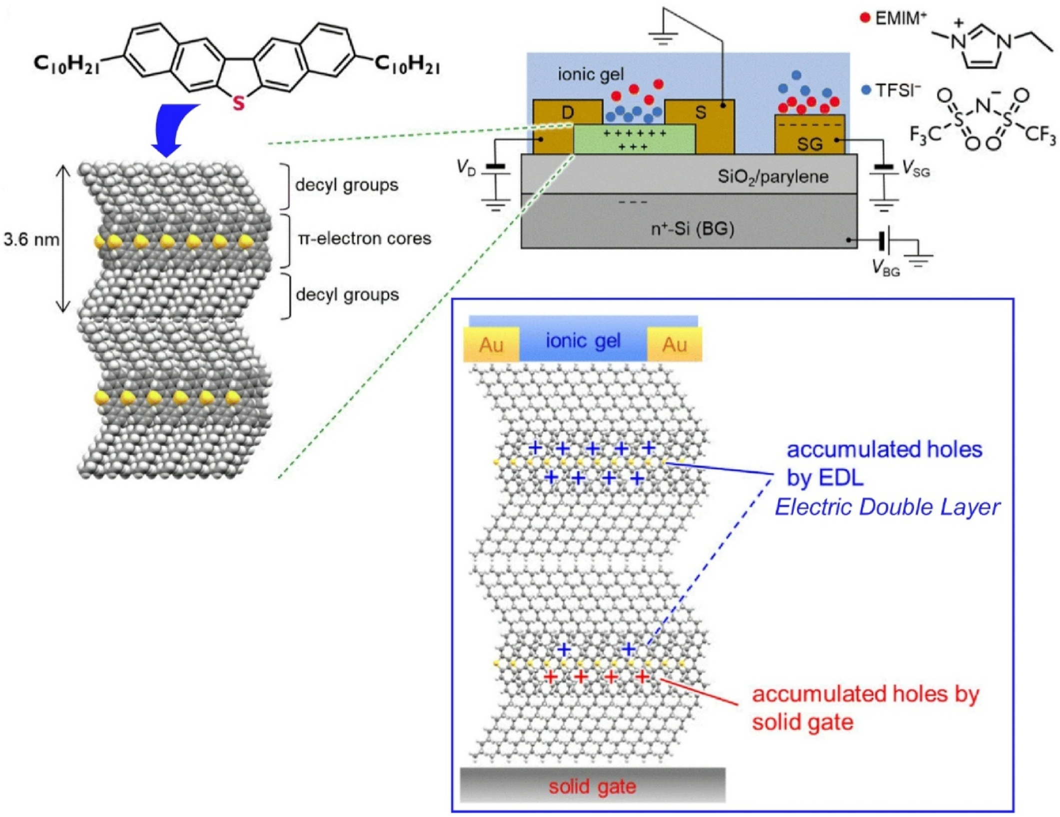

FIGURE 10 Device structure with solid gate and ionic gel gate on the bottom and top surfaces, respectively, of bimolecular-thick single crystals of p-type organic thin-film transistors. Reproduced with permission.[102] 2023, Royal Society of Chemistry.

responsive dynamic processes for smart molecular systems and devices.

Nanoarchitectonics of surfaces allows the development of materials that combine versatile functions. Tao and co-workers have created fluorine-free UV-responsive materials for oil/water separation materials and dye degradation (Figure 11).[104] Cellulose, silicon dioxide, titanium dioxide, and stearic acid were used to create the superhydrophobic coatings. An environmentally friendly fluorine-free superhydrophobic coating was created. In addition, 3-aminopropyltrimethoxysilane was used to provide adhesive properties. These nanoarchitectonics products can be coated on cotton fabrics by a simple dip coating method. The coated cotton fabrics exhibited excellent superhydrophobicity and self-cleaning properties. They were able to withstand mechanical performance tests such as scrubbing and immersion in boiling water. The coated cotton cloth was used not only for separating heavy oil and light water mixtures, but also for separating surfactant-stabilized oil-in-water and oil-in-water emulsions. Wettability changes from superhydrophobic to superhydrophilic under UV irradiation. In addition, after UV irradiation, methyl blue can be decomposed. This approach will contribute to the development of intelligent materials that perform multiple functions. It is also expected to have high potential in its industrial production.

By intentionally nanoarchitectonizing complex structures on surfaces, materials can be developed that have a combination of incompatible properties. For example, stretchable, self-powered sensors are of great interest in the next generation of wearable electronics, but they must combine the properties of several materials. Zhang, Bowen, and co-workers have developed a biomimetic soft rigid hybrid strategy to construct a new form of piezoelectric sensor with high flexibility, high performance, and stretchability (Figure 12).[105] Droplet-shaped hierarchical ceramics were fabricated by freeze casting on superhydrophobic surfaces. This hierarchical droplet-shaped ceramic structure effectively provides a rigid element. The unique arched surface and rounded corners of the unique droplet shape can relieve stress concentration. To ensure electrical connection of the piezoelectric phases during stretching, the patterned liquid metal acts as a soft circuit. In addition, silicone polymers

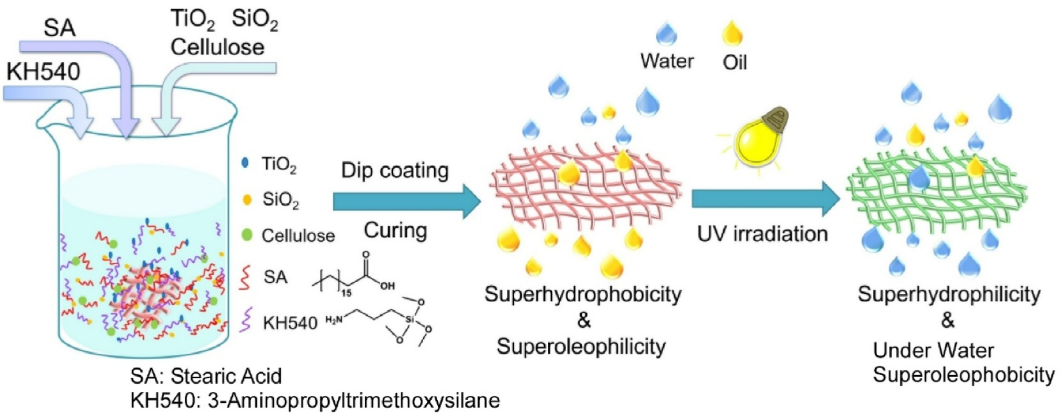

FIGURE 11 UV-responsive materials for oil/water separation materials fabricated with cellulose, silicon dioxide, titanium dioxide, stearic acid, and 3-aminopropyltrimethoxysilane. Reproduced with permission.[104] 2022, Oxford University Press.

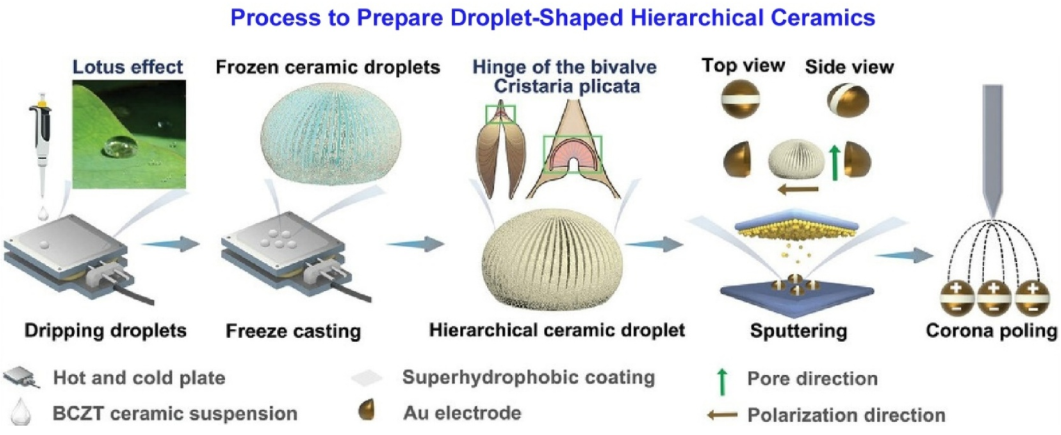

FIGURE 12 Fabrication of droplet-shaped hierarchical ceramics with unique arched surface and rounded corners. Reproduced under terms of the CC-BY license.[105] 2024, Wiley-VCH.

with optimized wettability and extensibility are introduced as soft components. This structure forms a strong mechanical interlock with hierarchical ceramics. Nanoarchitected stretchable sensors can be used for healthcare applications. For example, they were used for wireless gesture recognition and to assess the progression of knee osteoarthritis. The high potential in the field of stretchable and flexible sensors for healthcare, e-skin, and wearables was demonstrated. This tactic breaks the current trade-off between piezoelectric activity and stretchability, which has been difficult to achieve with traditional processing strategies. It will provide useful hints for the development of future stretchable devices for soft robotics and healthcare.

With rapid advances in human-machine interaction and voice biometrics, soft mechanical sensors that can detect complex dynamic signals are desired. Lu and co-workers proposed a hydrogel-based soft mechanical sensor that skillfully utilizes layered nanoarchitectonics to record a wide range of human-related dynamic signals (Figure 13).[106] Mechanical acoustic signals play an important role in human-machine interaction and human health diagnostics. Iontronic dynamic sensors are intended to monitor a wide range of human-related dynamic signals, including complex frequency sound signals such as the human voice and the sound of musical instruments. The nanoarchitectonics combines a preloaded design strategy with an iontronic sensing mechanism. The sensing module is a multilayered structure made of a polyethylene terephthalate film coated with a silver electrode film, a resin/elastomer ring frame, a microstructured hydrogel film, and an elastomer base coated with a gold electrode film. By adjusting the parameters of the preload and microstructure hydrogel, it can be precisely tuned to meet the desired requirements. The sensor can record instrumental sounds with high fidelity, from simple pure tones to melodic tunes. The skin-wearable sensor can also be used for voice-activated remote control of toy cars. This demonstration could make a significant contribution to voice user interface applications in human-machine interaction.

5 | LIVING CELL LEVEL RESPONSE

One application of surface nanoarchitectonics to more complex functional systems is the determination of cell fate by spontaneous stimulation of the interface. In many cases, mechanical stimuli transmitted to cells are modulated by coating solid substrates with various mechanical properties or by creating nanostructures.[107–109] A recent advanced topic is the use of weak forces from spontaneously generated nanostructures at the liquid–liquid interface to control cells.[110,111] The last section discusses such examples.

Jia et al. have studied the behavior of stem cells at the liquid–liquid interface between water and fluorocarbons.[112,113] Adaptive biomaterials containing fibronectin inserted into protein nanosheets at the liquid interface have been found to promote neuronal differentiation of human mesenchymal stem cells. Stem cells and the microenvironment interact cooperatively to determine cell fate. Biomaterials are dynamically remodeled by stem cells. Furthermore, stem cells sense the changes and reflect them in cell fate decisions. Recently, Jia, Nakanishi, and co-workers investigated the effect of adaptive biomaterials based on two-dimensional networks of protein nanofibrils at the liquid–liquid interface.[114] Compared to flat protein nanosheets, networked biomaterials promote neural

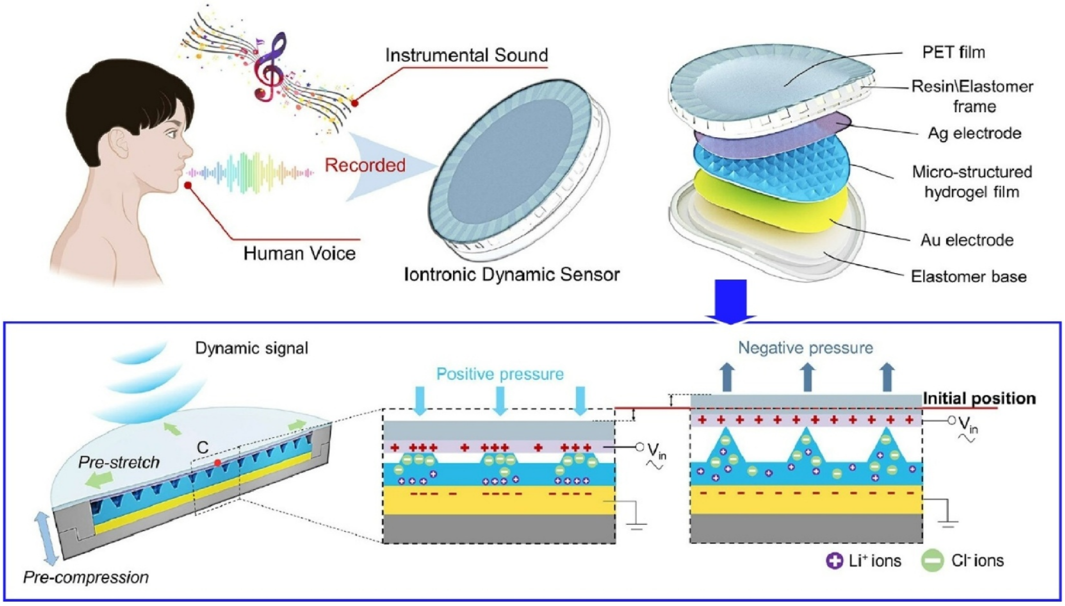

FIGURE 13 A hydrogel-based soft mechanical sensor with layered nanoarchitectonics for a wide range of human-related dynamic signals. Reproduced with permission.[106] 2024, American Chemical Society.

differentiation of human mesenchymal stem cells through a signaling mechanism involving focal adhesion kinases. In particular, lipid raft microdomains in the plasma membrane play a central role in the rapid adaptation of human mesenchymal stem cells to the dynamic microenvironment at the liquid interface (Figure 14). Lipid rafts internalize cell adhesion molecules and are involved in the process of mobilizing them to different cell membranes. Lipid rafts also function as enrichment platforms and support the integration of large signaling complexes. This role with lipid rafts allows cells to rapidly adapt to a constantly changing microenvironment. It is also suggested that focal adhesion kinase is one of the key mechanosensors at the adaptive liquid interface. Spatio-temporal regulation of focal adhesion kinase phosphorylation results in neural differentiation of human mesenchymal stem cells. These findings have major implications for regenerative medicine and tissue engineering. In particular, they provide the basis for dynamic interactions between cells and extracellular matrices and for understanding the biophysics underlying mechanotransduction. A variety of stimulus responsiveness could be incorporated into such systems by incorporating bioactive proteins and responsive polymers. The liquid–liquid interface will provide a valuable venue to guide the design of new adaptive biomaterials for applications in regenerative medicine and tissue engineering.

Perfluorocarbons and silicones, for example, form an insoluble interface with water, where they allow cell adhesion through protein nanolayers. However, these liquids could only control a narrow range of physicochemical parameters. Thus, they could not provide a variety of cell culture environments. To overcome such difficulties, Ueki, Nakanishi, and co-workers investigated cell culture at the liquid–liquid interface using water-immiscible ionic liquids (Figure 15).[115] Ionic liquids have tunable physicochemical properties and high solvation capacity. The tetraalkylphosphonium-based ionic liquid used is a non-cytotoxic ionic liquid. Human mesenchymal stem cells were successfully cultured at the interface between water and this ionic liquid. Elongation of the alkyl chains reduces the charge distribution of the cations, that

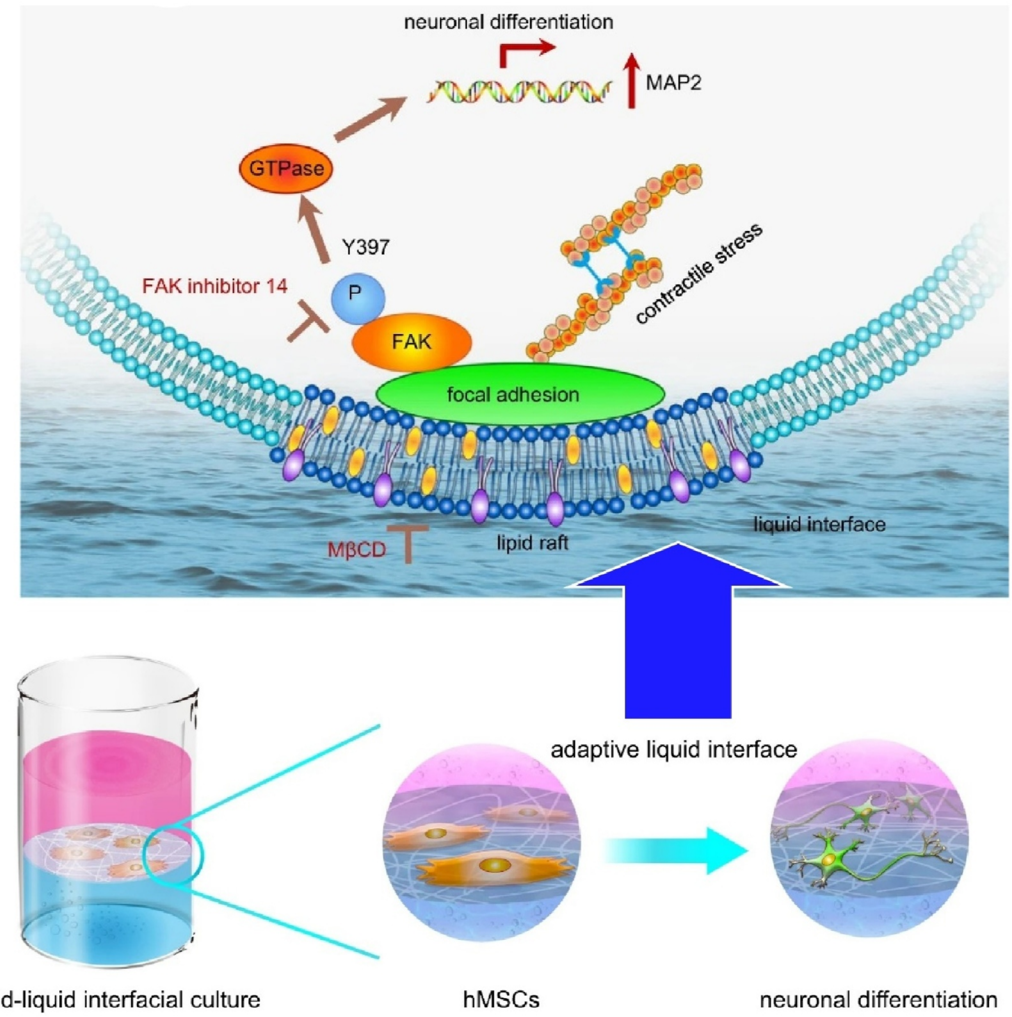

FIGURE 14 Neural differentiation of human mesenchymal stem cells promoted with networked biomaterials through a signaling mechanism involving focal adhesion kinases where lipid raft microdomains in the plasma membrane play a central role in the rapid adaptation of human mesenchymal stem cells to the dynamic microenvironment at the liquid interface. Reproduced under terms of the CC-BY license.[114] 2022, Springer-Nature.

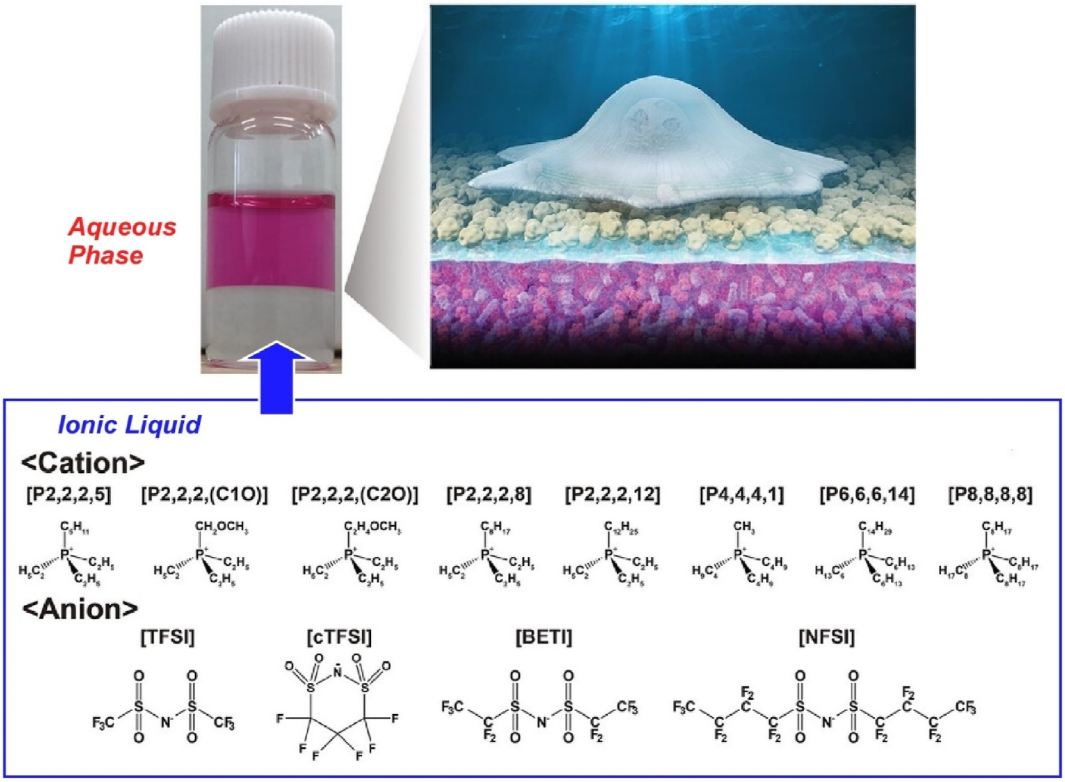

FIGURE 15 Cell culture at the liquid–liquid interface using water-immiscible ionic liquids. Reproduced with permission.[115] 2024, Wiley.

is, their ionicity, and the interface allows cell diffusion with a mature focal contact. Unlike fluorocarbons, ionic liquids can dissolve a wide variety of substrates and are therefore also suitable for altering the bulk mechanics of hydrophobic phases. The van der Waals interactions of the constituent ions of ionic liquids and the charge distribution of cations were tuned and their effects on protein nanolayer formation and cell adhesion were investigated in detail. It also has significant practical advantages. Compared to the conventional two-dimensional culture method using plastic dishes, its culture efficiency is much higher. Since the liquid can deform freely, cell resources can be recovered by a filtration process that does not require trypsin enzyme treatment. If this becomes possible, it will also lead to the complete automation of the cell culture process. Finally, it is expected to lead to the realization of an environmentally friendly cell culture method that does not produce plastic waste.

6 | SHORT SUMMARY AND PERSPECTIVES

In this review article, we summarize stimulus-response systems from the atomic and molecular level to the living cell level in terms of nanoarchitectonics at interfaces. For example, a stimulus-response system at the molecular level is a molecular machine. From the viewpoint of nanoarchitectonics, a system in which several molecular elements work in concert is attractive. When such a system is organized on a surface, the interlocking behavior can be observed. For example, a probe microscope stimulus can move several molecular gears in tandem. In terms of converting molecules, synthetic methods that are not possible with conventional organic chemistry, where the chemistry of molecules present on the surface is under an electron beam, can become possible. An example is the control of reactions by stimuli such as the application of local voltage from the tip of a probe microscope. Atomic manipulation with the tip of a probe microscope can also control magnetic topological states through spin polarization.

In nanodevices, there are molecular switches in which the switch part is a molecule and atomic switches in which the switch part is an atomic cluster. Examples have been reported in which device functions can be expressed by such dynamic nanoarchitectonics of atoms and molecules. Resistance change memory using silver ion conductive solid polymer electrolytes is an electrochemical atomic switch realized using organic materials. In atomic switches using porous polymers, the switching behavior transitions from volatile to nonvolatile in response to metal filament development. This can be changed from short-term memory to long-term memory by repeated voltage sweeps. In addition, quantization of conductance by an integer factor of single-atom point contacts is achieved in response to growth in Ag filaments in the polymer matrix. Atomic cluster architectonics makes device quantization possible. Field-mediated atomic switches for low bias stimuli have also been achieved. This mimics the field-mediated communication found in the cerebellum, heart, retina, and olfactory system. Nanoarchitectonics, which brings doping to thin films of organic semiconductors, also allows precise control of conductivity in conjunction with proton coupled electron transfer reactions widely used in biochemical processes. Molecular-level device design is also possible, in which gate functions are provided at both interfaces of crystalline sheets of organic semiconductors a few molecules thick.

Interfacial nanoarchitectonics with diverse components is useful for the construction of material-level stimulus-responsive systems. Photo-induced structural control of azobenzene derivatives and azobenzene polymers nanoarchitectonized on surfaces can be applied to photo-stimuli-responsive dynamic processes for smart molecular systems and devices. Nanoarchitectonics of surfaces can develop materials that combine a wide variety of functions. UV-responsive materials for oil/water separation and dye degradation have been developed. By intentionally nanoarchitectonizing complex structures on surfaces, materials can be developed that have a combination of incompatible properties. Hybrid strategies can also be used to create new forms of piezoelectric sensors that are flexible, high performance, and stretchable. There is an example of a hydrogel-based soft mechanical sensor made with layered nanoarchitectonics. This could contribute significantly to applications in voice user interfaces in human-machine interaction.

An application of surface nanoarchitectonics to more complex functional systems is the determination of cell fate by spontaneous stimulation of the interface. Cells are controlled using weak forces from spontaneously generated nanostructures at the liquid–liquid interface. Adaptive biomaterials based on two-dimensional networks of protein nanofibrils at the liquid–liquid interface promote neural differentiation of human mesenchymal stem cells through signaling mechanisms. Water immiscible ionic liquids can also be used to culture cells at the liquid–liquid interface. These nanoarchitectonics at the liquid–liquid interface will provide guidelines for designing new adaptive biomaterials for applications in regenerative medicine and tissue engineering. It will also lead to the realization of environmentally friendly cell culture methods that do not produce plastic waste.

As described above, a wide range of stimulus-responsive systems, from devices based on atomic and molecular movements to differentiation control by signal transduction in living cells, can be created by interfacial nanoarchitectonics. The abundance of choices should also make it possible to construct responsive material systems by combining them. Rather, the development of materials that can control such complex systems will be useful for the development of highly functional responsive material systems, such as those in living organisms. However, the more diverse the components and the more complex the structure, the more difficult the approach becomes. The experience and intuition of the experimenter, or the principled predictions of academia, may not be sufficient. Fortunately, mankind has rapidly developed artificial intelligence. The use of machine learning for materials design[116,117] and the concept of materials informatics[118–120] have become popular. The need to integrate nanoarchitectonics and materials informatics has also been proposed.[121] Such new information technologies will strongly support the development of responsive materials systems through nanoarchitectonics.

Another problem to be solved is the conversion to industrial applications. As we have shown in several examples, many of the interface stimulating materials from MANA have strong practical potential. It will also be important to determine how to translate the methodology of material creation by nanoarchitectonics into mass production. If the social demand for these materials is fully recognized, such development is expected to progress. I hope that this review article will play a role in stimulating such development.

AUTHOR CONTRIBUTIONS

Katsuhiko Ariga: Conceptualization (lead); funding acquisition (lead); writing—original draft (lead); writing—review and editing (lead).

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

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