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Review

Atom/molecular nanoarchitectonics for devices and related applications

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ABSTRACT

Fusion of nanotechnology with the other science disciplines including organic chemistry, supramolecular chemistry, and biotechnology creates a new conceptual paradigm, nanoarchitectonics. In this review article, we focus on recent contribution of the nanoarchitectonics concept on device fabrication. In these approaches, various materials such as organic semiconductor crystals, carbon nanotubes, graphene, and nanosheets are nanoarchitected by self-assembled monolayer technique, meniscus-driven crystallization, photochemical layer-by-layer process, ice resist lithography, vortex Langmuir-Blodgett method to various devices including atomic switch, artificial synapses, decision-making device, nonvolatile memory, multi-valued logic circuits, organic field-effect transistors, conductive cellulose nanopapers, organic photovoltaics, fuel cells, biocompatible batteries, and microbial biophotovoltaic cells.

Contents

Introduction

Indispensable targets in advancements of current technology are mainly related with energy production from new and less-explored resources [1–9], minimization of unnecessary emissions [10–14], environmental protections and sensing [15–19], high performance material/signal/information conversion [20–24], high-skill bio-treatment [25–31], and high-density and rapid information storages and transfers [32–34]. As recognized in sciences and technologies in these days, these targets will be accomplished mainly by fabrication with efficient and rational controls of their microscale and nanoscale structures. In fact, rapid progresses of microfabrication technology in late 20th century actually realized huge developments of device functions. So-called top-down-type approaches open many possibilities in miniaturized functional systems. Further sophistication of miniaturization processes to nanometer scales created a novel powerful concept, nanotechnology, which enables us to observe and fabricate even atomic-level (molecular-scale) structures [35–39].

However, success of miniaturization of functional systems such as devices might not be continued permanently only with fab-

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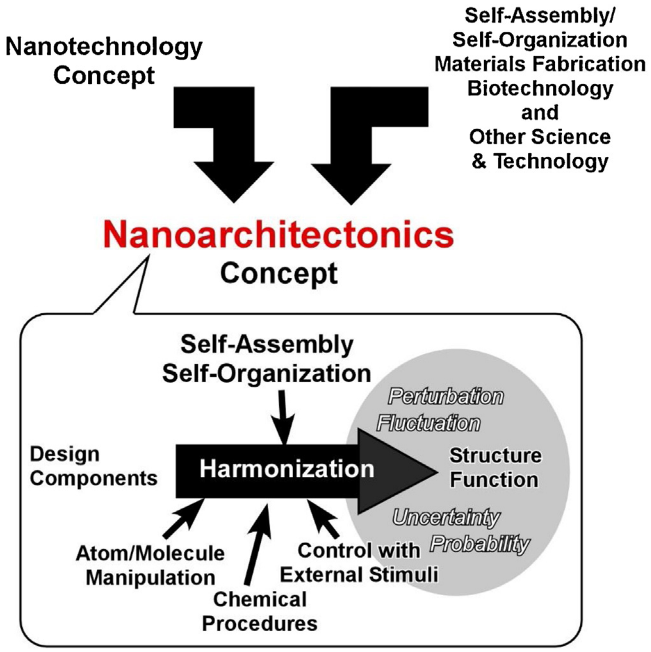


Fig. 1. Outline of nanoarchitectonics concept upon harmonization of various interactions and mechanisms including uncontrollable factors.

rication techniques on conventional materials such as silicon and semiconductor materials. In order to make breakthrough in developments of functional materials, systems, and devices, explorations on new materials and their precise structural regulations must be well combined with nanotechnological fabrication techniques. Conceptual fusion of nanotechnology with the other science disciplines including synthetic organic chemistry [40–45], supramolecular chemistry [46–55], and biology/biotechnology [56–64] is essential to make a paradigm shift to bottom-up-oriented approaches in developments of functional systems based on nanostructure unit motifs. This can be regarded as conceptual revolution from nano-technology to nano-architectonics [65,66].

A new conceptual terminology, nanoarchitectonics, was first proposed by Masakazu Aono at the 1st International Symposium on Nanoarchitectonics Using Suprainterations in 2000 [67,68] and was first used in a title of scientific publication by S. Hecht in 2003 [69]. The approaches by the nanoarchitectonics concept provide functional materials and systems by regulated arrangements of nanoscale functional units upon mutual interactions of unit components (Fig. 1). The nanoarchitectonics processes use synergic contributions and/or harmonization of various interactions and mechanisms such as chemical-reaction-based molecular modification, arrangement control of atoms and molecules, self-assembly/self-organization, structural rearrangement upon the application of various physical stimuli, and biological actions [70–72]. Because nanoscale phenomena often include dynamisms based on several uncertainties such as thermal fluctuations, quantum effects, and complicated mutual interactions [73,74], material functions may somehow become closer to wise-thinking biological systems [75–77]. These general concepts can share their methodologies with the various research fields, and therefore, application of the nanoarchitectonics concept has been proposed for a wide range of research approaches including nanofabrications [78–80], preparation of functional materials with regulated nanostructures [81–83], self-assembly/self-organization and supramolecular structural regulations [84–88], sensing [89–92], catalysis [93–95], environmental remediation [96–98], energy applications [99–102], and biological/biomedical issues [103–107].

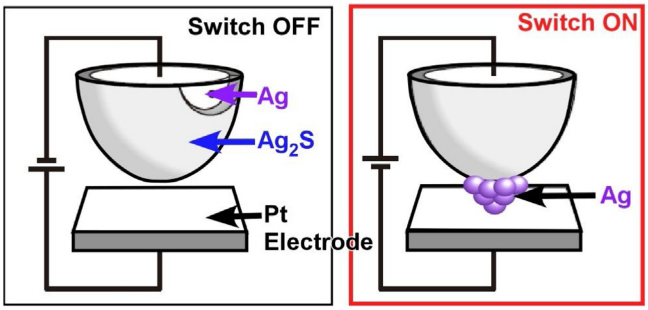


Fig. 2. An atomic switch where reduction of Ag^+ ion to Ag atom at the vicinity of the Ag_2S electrode causes formation of Ag clusters bridged between the electrodes (switching this device on).

Unlike simple self-assembled process in supramolecular chemistry, nanoarchitectonics approach can assembled various components in irregular and hierarchic ways. In addition, structural flexibility and ambiguity from thermal fluctuation and statistic effects can be included in the nanoarchitectonics approach. Therefore, functional systems and materials can be constructed through harmony of various interactions and complicated components.

In this review article, we focus on recent contribution of the nanoarchitectonics concept on device fabrication [108–110]. Research examples highlighted in this review article includes (i) devices based on motions and organization of atoms and ions as seen in atomic switches, (ii) improved device performances with organic semiconductor nanoarchitectires, (iii) organization of polymers and inorganic materials for better device properties, (iv) innovative fabrication methods for device nanoarchitectonics, and (v) possible challenges for bio-conjugations. Advanced miniaturization of devices makes distance between device technology and atom/molecular sciences much smaller. Importance of structure organization in micro and nano-scales sufficiently increases in device technology in these days. Introduction of the nanoarchitectonics concept into device technology becomes crucial for further development. In this review article, various devices such as switches, transistors, sensors, and energy converters are exemplified.

Nanoarchitectonics for atom-based devices

Regulation of atoms and molecules creates device-like functions in nanoscale regime. Electrical switching based on chemical reactions and atoms (ions) diffusion becomes possible with appropriate nanoarchitectonics designs. This switching mechanism is far different from physical-contact-based conventional switches in macroscopic scales. These switching systems nanoarchitected with atomic actions are called atomic switches [111]. A typical structure of atomic switch is illustrated in Fig. 2, which was pioneered by Aono and co-workers. Several atomic-level events including electrochemical reaction, diffusion, and precipitation at nano-level gap of two-electrodes (Ag_2S and Pt) result in controlled electrical communications between these electrodes. Reduction of Ag^+ ion to Ag atom at the vicinity of the Ag_2S electrode upon a negative bias application to the Pt electrodes causes formation of Ag clusters bridged between the electrodes. As the results, precipitation several atoms can switch this device on. Application of positive bias to the Pt electrodes induces oxidation of Ag atom to Ag^+ ion accompanying with dissolution of the formed switch. The latter process makes this device switched off.

Distinct differences of the atomic switches from conventional electrical switches do not appear only on their switching mechanisms, but also on their memory functions. It could be even said that potential capabilities of the atomic switch devices can be closer to biological synapses rather than man-made electrical switches. Ohno, Hasegawa, and co-workers demonstrated bio-like functions, short-term plasticity and long-term potentiation, using Ag_2S-based atomic switches through modification of the repetition time of an input pulse [112]. Low-frequency pulses with an interval of 20 s reversibly repeat appearances and disappearances of conductive bridges of Ag clusters between the electrode gap, corresponding to mimics of short-term plasticity. In contrast, stable long-lived higher-conductance cluster bridges are maintained upon application of high frequency input with a shorter 2 s interval time. It can be regarded as long-term potentiation. These behaviors are based on nanoarchitectonic formation of conductive bridges that is much different from simple physical contacts seen in conventional electrical switches. It was further demonstrated by Stieg and co-workers that networking of one billion interconnected atomic switches with silver nanowires realized a collective response to stimuli inputs as mimic of nanoarchitected neuromorphic device [113].

Krishnan, Tsuruoka, and co-workers investigated detailed behaviours of polymer-based atomic switches that possess poly(ethylene oxide) (PEO) between the electrodes to nanoarchitect gapless-type atomic switches [114]. Growing behaviours of conductive filaments within PEO matrix were evaluated microscopically in three types atomic switches with Ag/Ag–PEO/Pt, Ag/PEO/Pt, and Pt/Ag–PEO/Pt nanoarchitectures. Comparisons of these atomic switches with different mechanisms revealed several factors on switching operations. Self-assembly of the polymer films into lamellar nanoarchitectures. Inclusion of Ag^+ salt in the polymer matrix drastically alter ion conductivity and conductive Ag filament growth. Ag electrodes work as a supplier of Ag^+ ion and contributes metal filament growth. Based on these facts, practical application of polymer-based atomic switches as nonvolatile memory devices can be considered. The same research team also more advanced function of polymer-based atomic switch nanoarchitectures of Ag/PEO/Pt device motif [115]. The used polymer-based atomic switches exhibited multiple quantized conductance states which can develop novel multilevel memory devices. This concept leads to integer multiples, half-integer multiples, and fractional variations.

Operation concept of these atomic switches are included in more general concept of nanoionic devices, as explained by Terabe et al in their review article [116]. Working principles of the nanoionic devices are based on nanoscale (even in atomic scale) ion migration, accompanying structural rearrangements including crystal, cluster, filament, and interfacial structures. Therefore, nanoionic devices can be regarded as typical examples of nanoarchitectonics-based devices. The nanoionic device concept includes atomic switches and artificial intelligence systems by networking of atomic switches. Tsuchiya et al. recently developed decision-making functions using physical nanoionic device with dynamic adaptivity [117]. As illustrated in Fig. 3, a two-electrode (Pt thin film electrodes A and B) electrochemical cell with a Nafion H^+-conducting polymer electrolyte equipped with a potentio/galvanostat and a random number generator. Because H^+ is homogeneously distributed in the Nafion electrolyte in the initial stage, both the electrodes are equivalent without potential difference. Pulse current applications causes deviation from the equivalent state between the two electrodes because H^+ distribution becomes asymmetric upon electrochemical reactions. The resulting concentration modulation of H^+ and gasses in the Nafion layer originates alteration of potentials between the two electrodes. Therefore, pulse current application can train this nanoionic device with potential modulations. When positive potential was observed, a random number between 0 and 1 was generated to emulate that channel A was selected with assigned probability. According to the obtained results, the current pulse was applied to the electrode A. Repeated process adapted the system to results in right decision. Combination of this decision-making nanoionic device with the former described artificial synaptic atomic switches may mimic complex personality formation in humans.

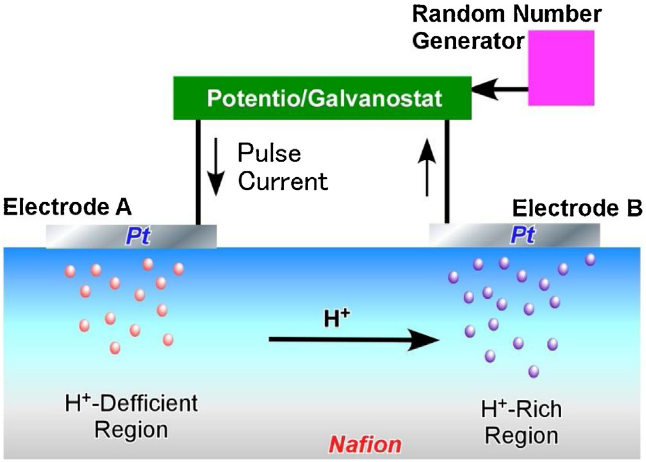


Fig. 3. A nanoionic device with dynamic adaptivity. Pulse current applications causes deviation from the equivalent state between the two electrodes and can train this nanoionic device with potential modulations.

This atomic-level nanoarchitectonics can be also utilized for control of the number of dopant atoms in solid electrolytes, resulting in materials with discrete electrical properties. Hasegawa and co-workers demonstrated atomic manipulation through ordered layer-by-layer precipitation using α-$Ag_{2+\delta}S$ nanodots [118]. The proposed atom nanoarchitectonics strategy is applicable to different nanoscale materials with properties regulated by the number of doping atoms/ions. It can be a new paradigm shift to create material synthesis based on regulation of single atom/ion-level transfer. Tsuchiya, Terabe, and co-workers reported atomic nanoarchitectonics approach on tuned doping to regulate electrical conductivity, magnetization, and magnetization and magnetoresistance in Fe_3O_4 thin film by Li^+ insertion and removal [119]. Tuning properties by the propsed strategy are much superior to known methods such as electrostatic carrier doping and would lead to developments of advanced high-density magnetic storage devices.

Nanoarchitectonics for molecule-based devices

For the nanoarchitectonics next to atomic scale organization, we need to think about molecules that are made from covalent linking of atoms. Therefore, nanoarchitectonics strategies for molecule-based devices are explained as the second category below. Because organic molecules have independent identities unlike continuous structures of inorganic materials, molecular nanoarchitectonics can create various modes of functional/structural controls including molecular manipulation, arrangement and orientation controls, and self-assembly/self-organization from molecular scale to macroscopic level. As molecular manipulation at very small level, Minamitani, Takagi, and co-workers successfully manipulated a single iron phthalocyanine molecule on a Au(111) electrode in sub-angstrom scale by a tip of scanning tunnelling microscope (STM) as a counter electrode (Fig. 4) [120]. Upon precise approach of the STM tip, the position of Fe^{2+} ion within the phthalocyanine molecular frame can be controlled, resulting in tuning Kondo coupling between the molecular spins and the Au electrode. This Hamiltonian manipulation in a single-molecule quantum dot regulates the strong Kondo couplings over the weak-coupling regime governed by spin-orbit interaction in the molecule. This exhibits the spectral crossover from the Kondo- to spin-orbit-interaction-dominant regimes reversibly. This example demonstrates high possibility to

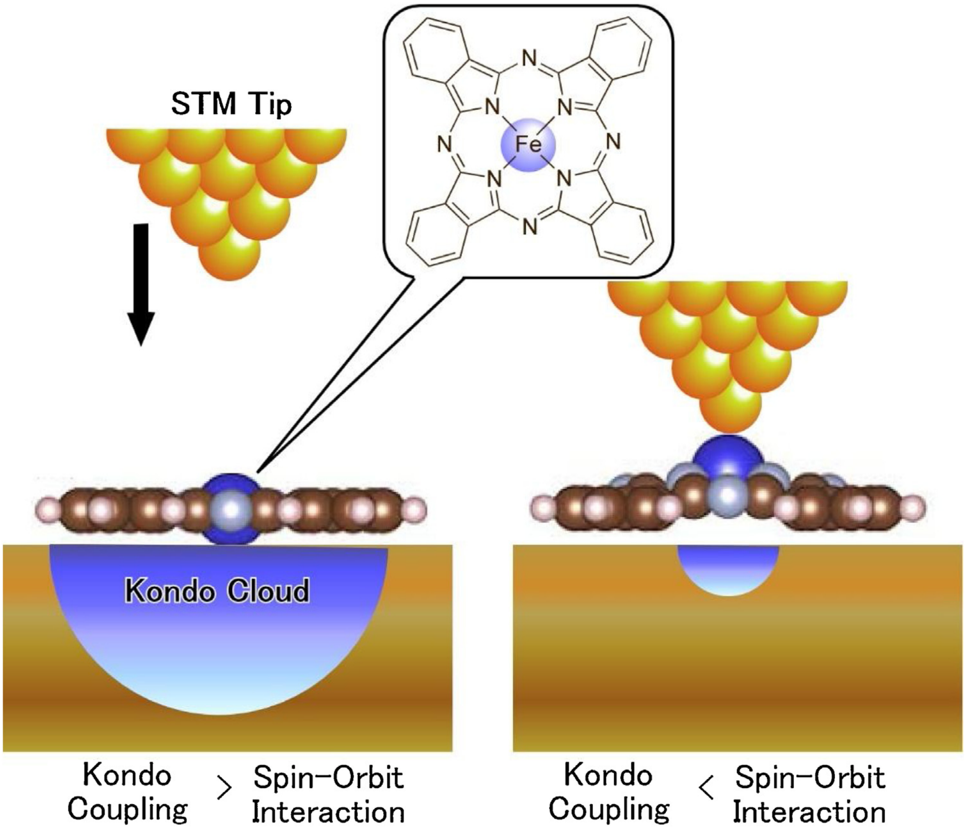


Fig. 4. Sub-angstrom-scale manipulation of a single iron phthalocyanine molecule on a Au(111) electrode in by a tip of scanning tunnelling microscope (STM) to regulate the strong Kondo couplings over the weak-coupling regime governed by spin-orbit interaction in the molecule.

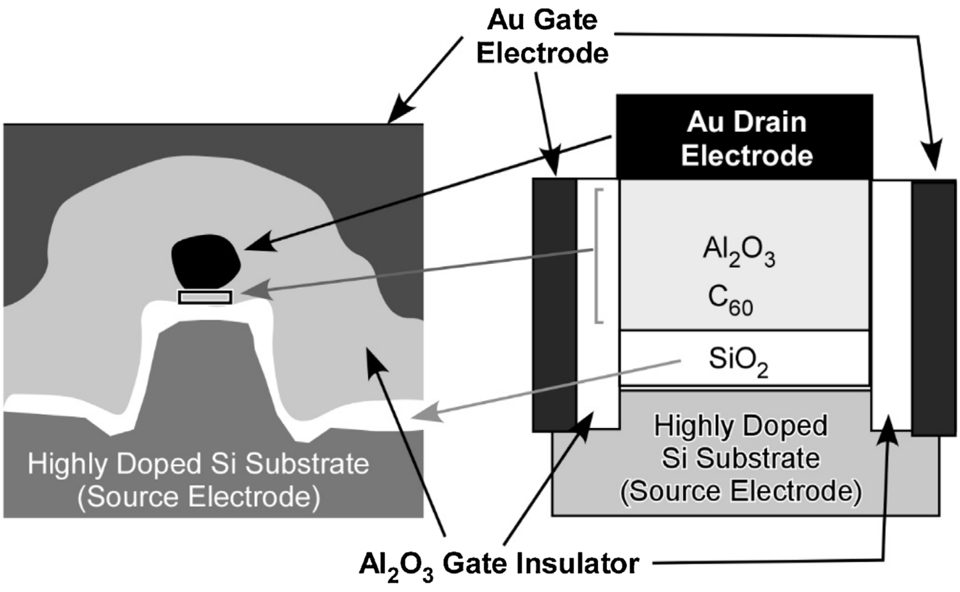


Fig. 5. A vertical resonant tunnelling transistor using molecular C_{60} quantum dots with a large ON/OFF ratio of the drain current (10^4).

control quantum phase transition by sub-angstrom-level molecular manipulations.

Hayakawa et al proposed nanoarchitectonics approach to fabricate vertical resonant tunnelling transistors using molecular C_{60} quantum dots [121]. As illustrated in Fig. 5, molecularly dispersed C_{60} units were embedded between Al_2O_3 and SiO_2 layers sandwiched vertically by source and drain electrodes. Further fabrication of gate insulator layers and gate electrodes completed vertical resonant tunnelling transistor structure. The fabricated structural motif works as a double tunnel junction with stepwise drain currents. The latter property is created through resonant tunnelling upon the discrete molecular orbitals. Its ON/OFF ratio of the drain current becomes 10^4 that is much higher than those reported for conventional molecular devices and monomolecular layer devices. The proposed device nanoarchitectonics would be a promising strategy for highly integrating molecular functions

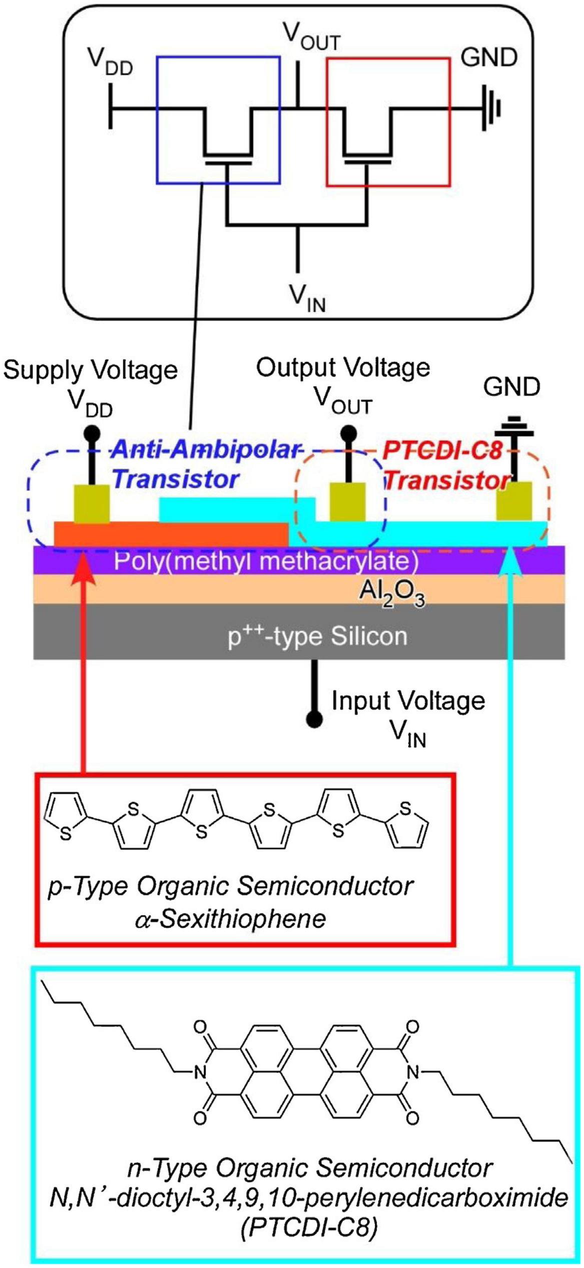


Fig. 6. A side-by-side arrangement of organic anti-ambipolar transistor with p-n junction and conventional transistor (PTCDI-C8 transistor) with *n*-type organic semiconductor.

in future complementary metal-oxide-semiconductor (CMOS) devices.

As examples of transistor architectonics, Wakayama and co-workers demonstrated fabrication of multi-valued logic circuits through side-by-side arrangement of organic anti-ambipolar transistor with p-n junction with *p*-type *α*-sexithiophene (α-6 T) and *n*-type *N*,*N*′-dioctyl-3,4,9,10-perylenedicarboximide (PTCDI-C8) semiconductors and conventional PTCDI-C8 transistor transistor (Fig. 6) [122]. When the gate voltage is low, current mainly goes through the anti-ambipolar transistor. Increase of the gate voltage induces balanced current distributions between the two kinds of transistors. Further increase of the gate voltages then results in sufficient reduction of the current at the side of the anti-ambipolar transistor. These changes create three values of input-output relations (0, 1/2, and 1), leading to multi-value switching. All these operations can be done under ambient conditions at room temperatures with sufficient stability and reproducibility.

Molecular nanoarchitectonics on design and synthesis of building blocks for electronic devices are crucial as reviewed by Takimiya and Nakano [123]. They exemplified importance of molecular designs of thiophene-fused naphthalene diimide molecules as electron deficient π-functional components including namely naphtho[2,3-*b*:6,7-*b*′]dithiophene diimide and naphtho[2,3-*b*]thiophene diimide. Advantages of these molecular building blocks are (i) low-lying energy levels of lowest unoccupied molecular orbitals (LUMO) and (ii) friendly functionalizability of the thiophene α-positions for further conjugations. Utilities of the synthesized thiophene-fused naphthalene diimide molecules were demonstrated as new electron deficient π-functional building blocks for organic electronic devices. These molecules are also useful as infrared dyes and electron acceptors for charge-transfer salts as well as building blocks for supramolecular nanoarchitectonics.

Okamoto and co-workers synthesized V-shaped organic semiconductors, oxygen- and sulfur-bridged bianthracene, which have bent structures based on the strong dispersion energy according to theoretical calculations (Fig. 7A) [124]. These bent structures are important for dense packing arrangements in their herringbone-packing motifs. The formed dense packing leads to an attractive intermolecular overlap, resulting in efficient electron transport due to well-controlled transfer integral. Evaluations on their performances on transistor configurations reveal that sulfur-bridged molecular nanoarchitecture for V-shaped semiconductors is more appropriate for two-dimensional carrier-transport than that with oxygen-bridged structural motif. Okamoto, Takeya, and co-workers also investigated performances of N-shaped organic semiconductor molecules (Fig. 7B) [125]. The synthesized zigzag N-shaped π-electron cores with long alkyl chains exhibited enhanced phase transition temperature from their crystalline phase because of significantly high chemical and thermal stability of the cores. The N-shape nature of semiconductor would suppress unfavourable molecular torsional motions. Field- effect transistor performances of their solution-crystalized samples indicated high hole mobility up to 20 cm^2/Vs. The proposed molecular nanoarchitectonics design for organic semiconductors satisfies several demands including processability, chemical stability, structural stability against thermal disturbances, and high charge carrier mobility.

Shishido, Mitsui, Takeya, and co-workers proposed importance of suppression of molecular vibrations of organic semiconductor layers for improved performances of organic devices [126]. They prepared single-crystal organic field-effect transistors on a flexible substrate and investigated effects of mechanical bending on charge mobility (Fig. 8). Uniaxial compression of crystal lattice by bending actually improved charge transport. Interestingly, only 3% strain induced 70% increase of charge mobility. Effect of band structure changes upon static structural changes of the organic crystals were estimated to be too small to explain the observed increases of charge mobility. Deeper analyses suggest that crucial factor of the mobility enhancement would be suppression of thermal fluctuations of individual semiconductor molecules. Compression of the crystals reduces the vibration of the semiconductor molecules, which significantly suppresses dynamic disorder. This mechanism is unique particularly for soft crystal systems with organic semiconductors unlike conventional inorganic devices. In addition, the observed large shifts of charge mobility against small mechanical changes would be useful to nanoarchitect ultrasensitive strain sensors for soft robotics applications.

As seen in the above-mentioned examples, two-dimensional layers of organic semiconductors can work as an ideal platform for electronic device applications. For further developments including practical applications and industrial production, one big challenge is large scale (large areal coverage) production of

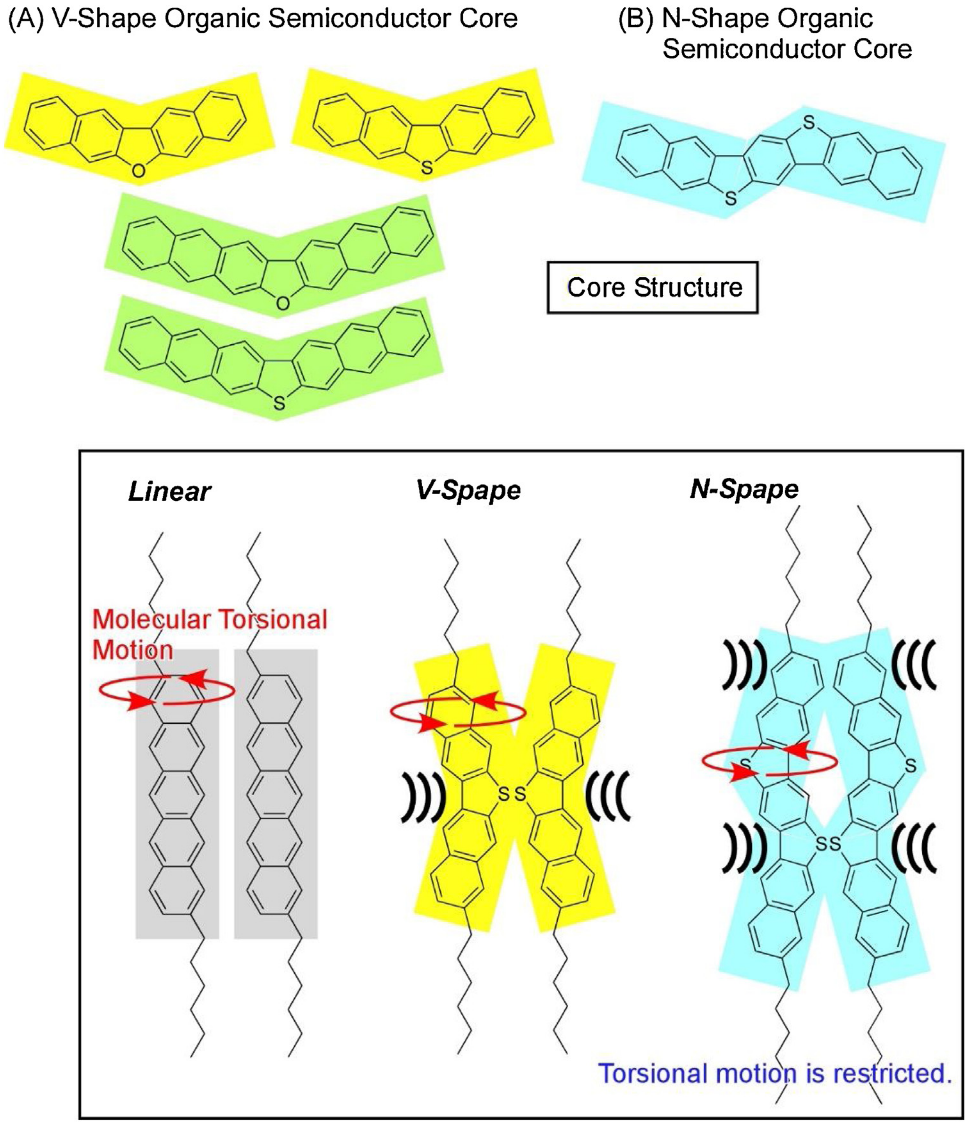


Fig. 7. (A) V-shaped organic semiconductor cores; (B) N-shaped organic semiconductor core. Uunfavourable molecular torsional motions would be suppressed in crystals of these V-shaped and N-shape organic semiconductors.

Fig. 8. Investigation on effects of mechanical bending on charge mobility in a single-crystal organic field-effect transistor of organic semiconductor to prove the importance of suppression of molecular vibrations of organic semiconductor layers for improved performances.

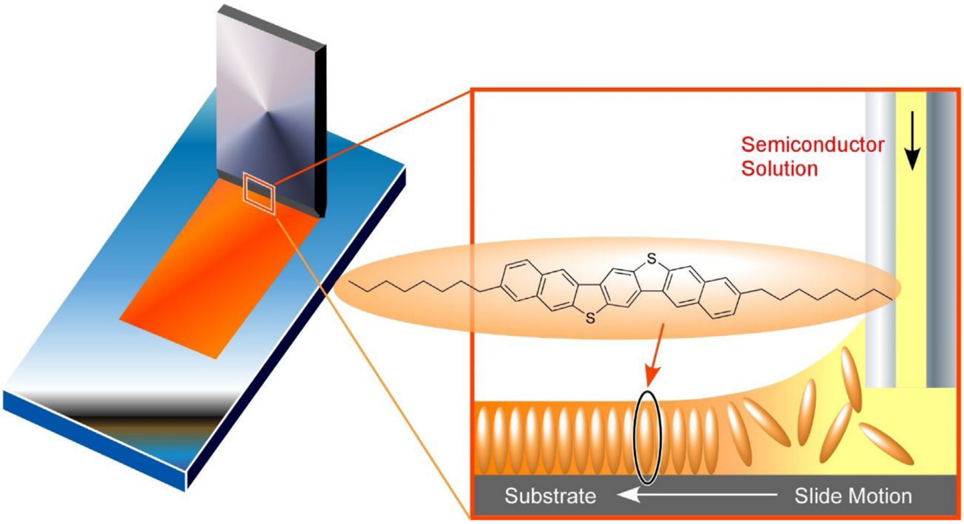


Fig. 9. A novel production way of wafer-scale, layer-controlled organic single crystals of organic semiconductor upon a meniscus-driven solution crystallization technique.

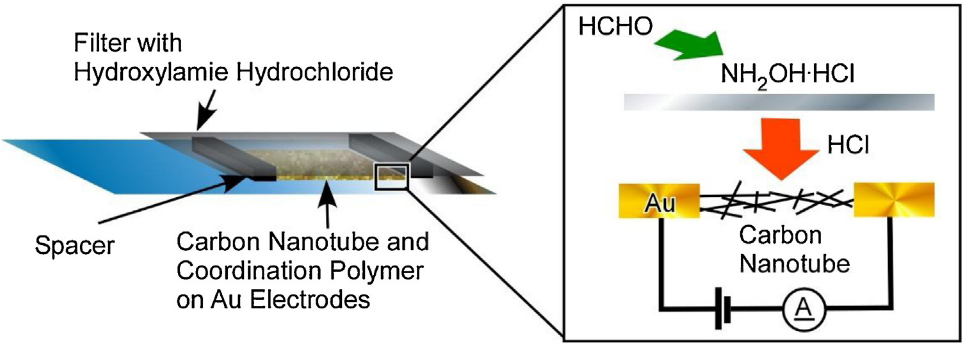


Fig. 10. A sensor device for sub-ppm-level formaldehyde detection on the basis of dynamic reaction and doping to single-walled carbon nanotubes. Formaldehyde, dynamically reacts with hydroxylamine to release hydrochloric acid, resulting in conductivity enhancement trough injection of hole carriers into semiconducting single-walled carbon nanotubes.

homogeneous two-dimensional single crystals. Okamoto, Takeya, and co-workers recently reported a novel production way of wafer-scale, layer-controlled organic single crystals with demonstration of high-speed circuit operation [127]. As illustrated in Fig. 9, meniscus-driven solution crystallization technique was optimized to achieve the large areal coverage of the layer-controlled two-dimensional single-crystalline films. Tuning of the operations enables selective preparation of monolayers, bilayers, and trilayers of single crystals of organic semiconductors in wafer-scale coverage. Estimated channel width-normalized contact resistance through the transmission line method is extremely low. Fabricated diode-connected bilayer organic field-effect transistor showed a rectifying capability higher than those commonly used in the wireless communication of radio frequency identifier tags. The reported approach would have important contributions to development of high-speed organic electronic devices.

Using crystalline nanoarchitectonics on organic single-crystal semiconductors, Watanabe, Takeya, and co-workers investigated coexistence of coherent charge transport and ultra-long spin relaxation time [128]. A linear relationship between these two relaxation times was confirmed by electron spin resonance spectroscopy and magneto-transport measurements over a wide temperature range. The obtained results imply a micrometre-scale spin diffusion length that are useful in organic single crystal nanoarchitectures for spintronic devices. Okamoto, Takeya, Yamaguchi, and co-workers used a boron-stabilized triphenylmethyl radical for organic Mott-insulator transistors operatable at room temperature [129]. Molecular nanoarchitectonics on organic neutral π-monoradicals leads to balanced ambipolar carrier transport capability. The designed boron-stabilized planar neutral π-radicals possess significant spin delocalization nature for excellent thermal stability and resistance toward atmospheric conditions. Solution crystallization method provided two-dimensional single crystals with herringbone-like packing nanoarchitectures. Characteristics of ambipolar transport having balanced mobility between electrons and holes are beneficial for organic Mott-insulator transistor at room temperatures.

Yagi and co-workers employed molecular nanoarchitectonics on Janus-type dendritic organoiridium(III) complex with hole and electron-transporting parts [130]. Sky-blue photoluminescence with a relatively high photoluminescence quantum yield of the facial complex isomer was observed even from its neat film states. It is originated from suppression of unfavourable aggregation of the phosphorescent cores by dendron moieties. Because the dendron parts also improve solution processability, non-doped organic light emitting diode with layered structures with emitting layer of the synthesized complex were easily prepared. Molecular nanoarchitectonics strategy with Janus-type organoiridium(III) complex is advantageous for solution-processed organic electronic devices. Traditional approach of molecular nanoarchitectonics, self-assembled monolayer (SAM) method, is common useful strategy. For example, Yamamoto and co-workers fabricated field effect transistor with self-assembled monolayer of tetrathiafulvalene [131]. Chemical doping with

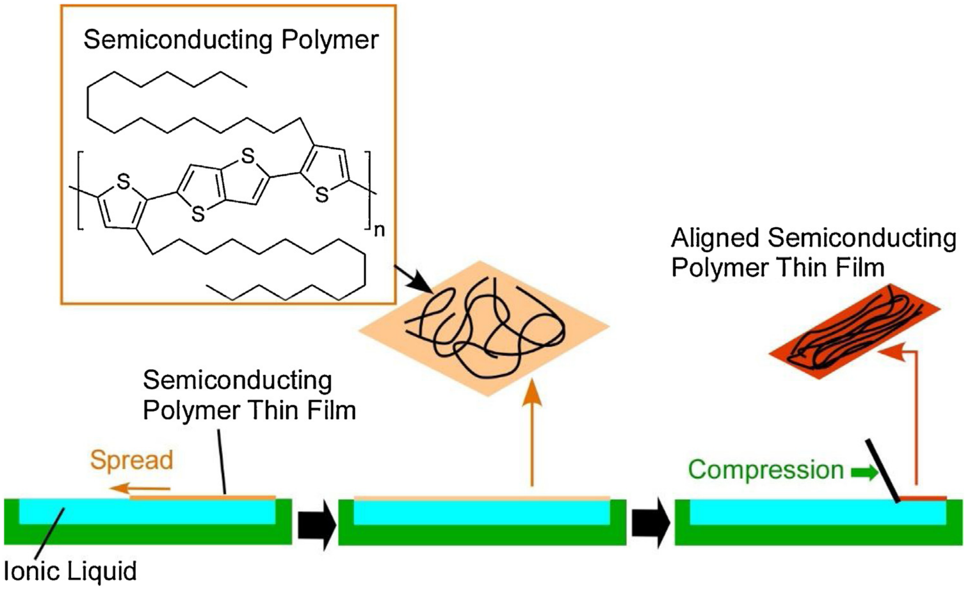


Fig. 11. Preparation of a highly oriented ultrathin film of semiconducting polymer compressed at the interface between air and ionic liquid that can be done at sufficiently high temperature.

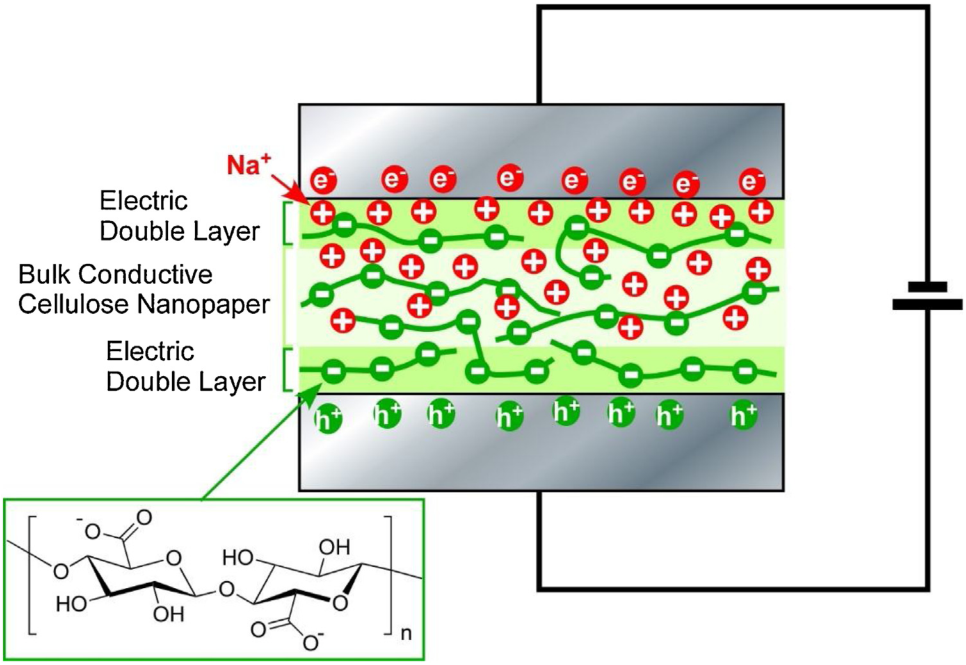


Fig. 12. A low voltage organic transistor with an ionic conductive cellulose nanopapers that can work as high-capacitance dielectrics and intrinsic ionic conductor in all-solid dielectrics.

2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane makes it as an ambipolar device. The resulting direction of gate voltage shifts was opposite to doping of conventional organic field effect transistor devices, which suggests a Mott field effect transistor. Suda proposed a novel way for photo-controllable molecular devices via self-assembled-monolayer-based nanoarchitectonics in his review [132]. Electronic properties can be modified through molecular dipoles and arrangements at interfaces of the self-assembled monolayers. Therefore, photo-controlled modifications of molecular dipoles at self-assembled monolayer interfaces enables photo-controllable molecular devices.

To summarize this section, it is found that sophisticated device performance can be found not only in a single molecule, but also in their nanoarchitected molecular assembly. Shaping and architecting functional molecules into highly topological, ordered structures would be a key engineering for maximizing their unique functionalities and for in-depth understandings in electronic properties in molecular devices.

Nanoarchitectonics for polymer-based devices

As compared with small-molecular-weight molecules and their assemblies, structures and properties of polymers and polymer

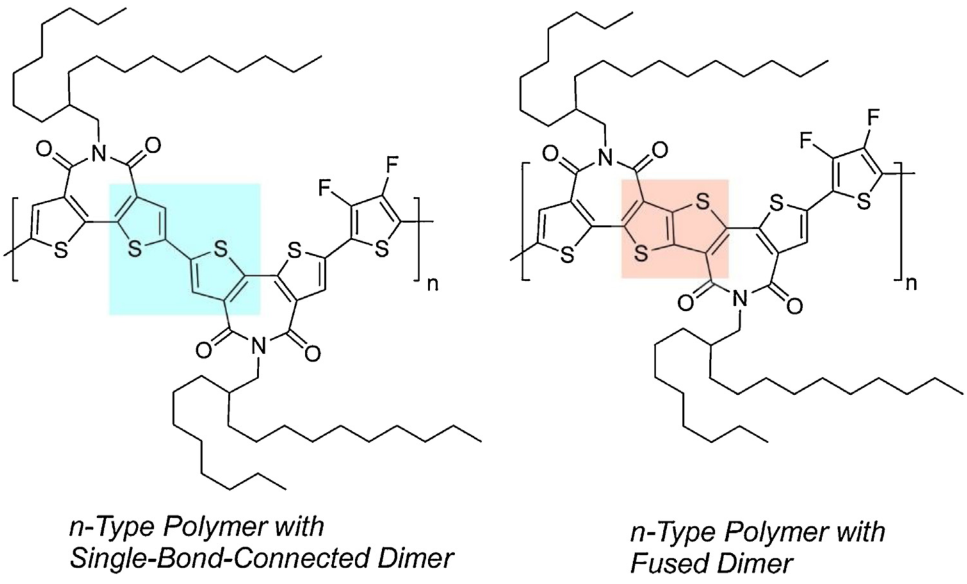


Fig. 13. Bithiophene-imide-based *n*-type polymers for organic thin film transistors: single-bond-connected bithiophene imide (left) and fused dimer of bithiophene imide (right).

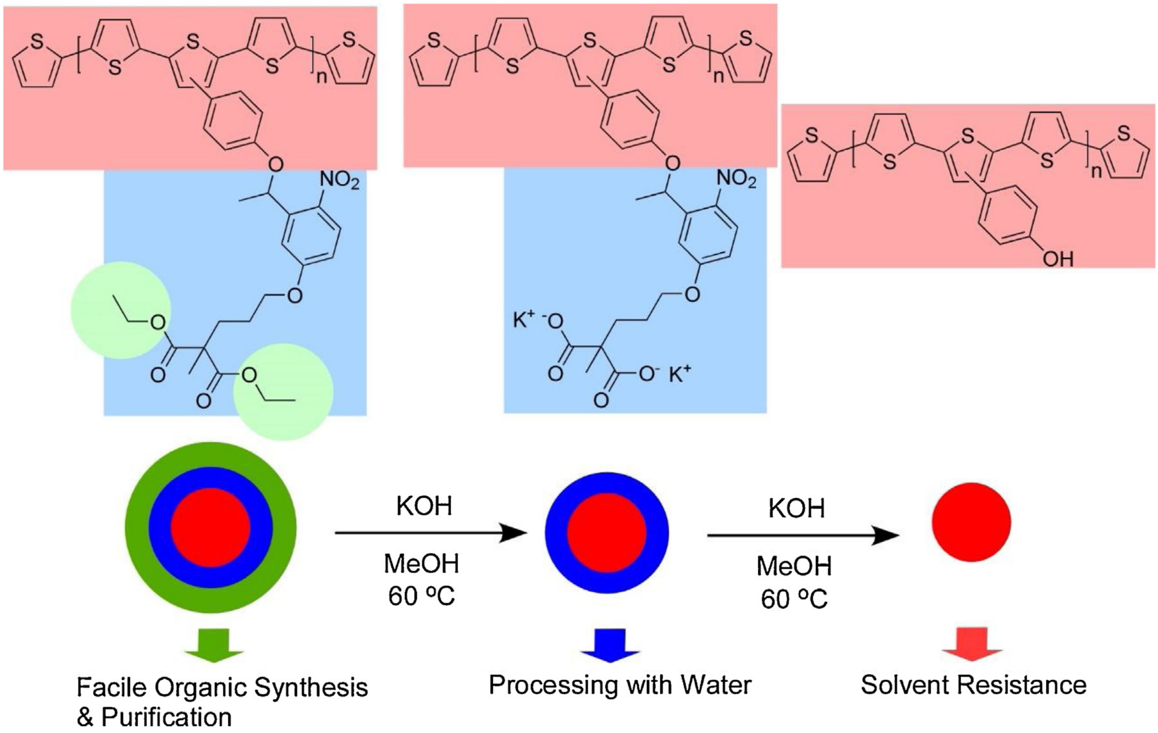


Fig. 14. Polythiophene-based conjugate polymers with multi-step cleavable side chain: (i) The initial form is soluble in organic solvents for facile organic synthesis and purification; (ii) The second form is water-soluble advantageous for water-based printing process: (iii9) the final form is a target electronic materials with solvent-resistant capability.

assemblies have somehow irregular natures and certain structural ambiguity. Unlike small molecules, linked unit parts in polymers have sometimes motional limitation and cannot easily form regular crystal structures. Therefore, functions upon dynamic changes with irregularity and flexibility are often highlighted in polymer-based functional systems such as polymer-based optoelectronic devices. Nanoarchitectonics approaches including certain dynamisms would have importance in designs and fabrications of polymer-based devices. Ishihara et al developed highly sensitive sensor device for sub-ppm-level formaldehyde detection based on dynamic reaction and doping to single-walled carbon nanotubes (Fig. 10) [133]. The sensor device was nanoarchitected by mixing of hydroxylamine hydrochloride and single-walled carbon nanotubes that was debundled by metallo-supramolecular polymer to increase sensitivity. Target gas, formaldehyde, dynamically reacts with hydroxylamine to release hydrochloric acid. The resulting hydrochloric acid gas injects hole carriers into semiconducting single-walled carbon nanotubes. Detection of formaldehyde can be sensitively carried out though monitoring conductivity shifts by an ohmmeter. Optimized nanoarchitecton-

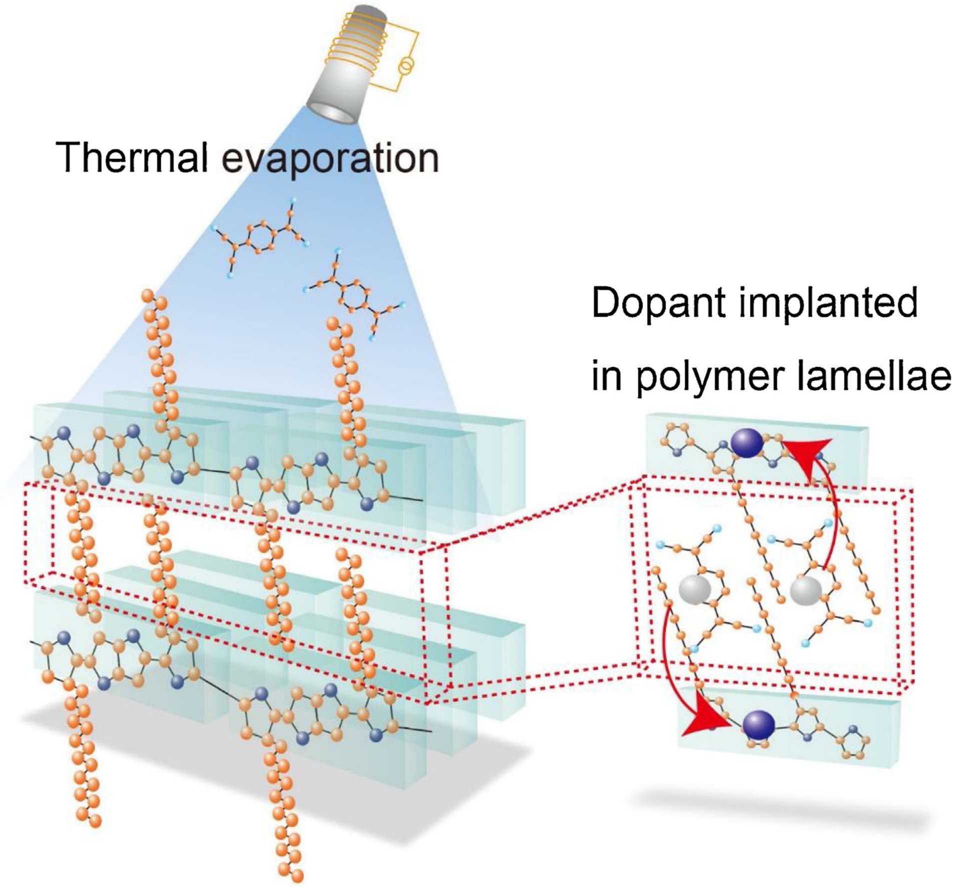


Fig. 15. Schematic illustration of solid-state doping method. An acceptor dopant that is thermally evaporated directly onto the top of semiconducting polymer thin films diffuses into the entire bulk of semiconducting polymer, and resides within the polymer lamellae.

ics construction of the systems resulted in excellent sensitivity to formaldehyde with a limit of detection of 0.016 ppm.

Conducting and semiconducting polymers have been used for a wide range of applications including energy, environmental, and device usages. Their electronic properties have significant dependences on their structures, conformation, orientation, and arrangements. Therefore, devices with conductive and semiconducting polymers can be said to be nanoarchitectonics-dependent. Yamashita, Takeya and co-workers demonstrated fabrication of high-performance polymeric organic field-effect transistors through forming highly oriented films of polymeric semiconductor compressed at the interface between air and ionic liquid (Fig. 11) [134]. Unlike water-based conventional Langmuir-Blodgett (LB) method, use of ionic liquid as subphase has crucial advantages extremely low vapour pressure even at high temperatures. Therefore, the proposed method affords polymer materials to have significantly high freedom of motions to align the polymer chains with supressing their intrinsic aggregative nature. Thin film preparation of poly[2,5-bis(3-hexadecylthiophen-2-yl)thieno(3,2-*b*)thiophene] was performed at 120 °C slightly above its liquid-crystal transition temperature. The film spread on the ionic liquid (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) was then compressed laterally and annealed, resulting in uniaxially align the polymer main chains within the film. The well-oriented films transferred onto a device surface exhibited highly-anisotropic charge-transport properties with an excellent field-effect mobility up to 10 cm^2/Vs.

Li and co-workers reported molecular nanoarchitectonics of balanced design of co-polymers with poly (amic acid) and polyimide moieties for high-performance flexible organic electronics [135]. The copolymers possess the phenyl rings and alicyclic rings with high chain packing density for improved insulating properties and polar groups such as —COOH and —CONH with advantageous natures in molecular packing and charge transport. Optimized balance of these moieties results in excellent dielectric contributions for flexible organic thin-film transistors with good performances including high charge mobility, low operation voltage, and outstanding stability.

Huang and co-workers developed ionic conductive cellulose nanopapers that were applied for low voltage organic transistors (Fig. 12) [136]. The prepared cellulose nanopapers can work as high-capacitance dielectrics and intrinsic ionic conductor in all-solid dielectrics. During oxidation of nanocellulose by (2, 2, 6, 6-tetramethylpiperidin-1-yl) oxidanyl, sodium ions are migrated that lead to ionic conductivity of cellulose nanopapers. Low-voltage flexible organic field-effect transistors were actually demonstrated using these materials as both the gate dielectric and substrate. In addition, organic complementary inverters based on ionic conductive cellulose nanopapers showed low operating voltages with voltage transfer characteristics.

Woo, Guo, and co-workers synthesized bithiophene-imide-based *n*-type polymers for organic thin film transistors and all-polymer solar cells [137]. The fused dimer of bithiophene imide units exhibited smaller band gap, lower LUMO, and higher crystallinity than single-bond-connected bithiophene imide dimer (Fig. 13). In addition, the fused analogue has a good electron mobility. The synthesized polymers were blended with the polymer donor for all-polymer solar cells that showed excellent power con-

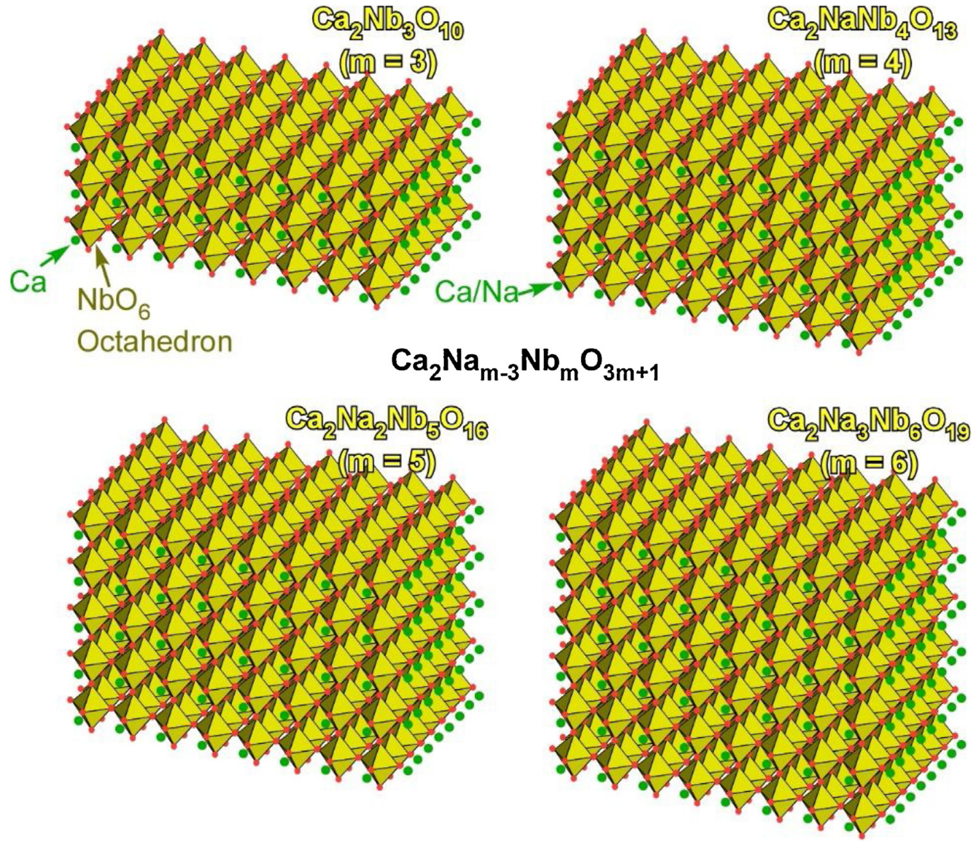


Fig. 16. Two-dimensional perovskites with high-κ ferroelectricity through atomic layer engineering using perovskite nanosheets ($Ca_2Na_{m-3}Nb_mO_{3m+1}$; m = 3–6).

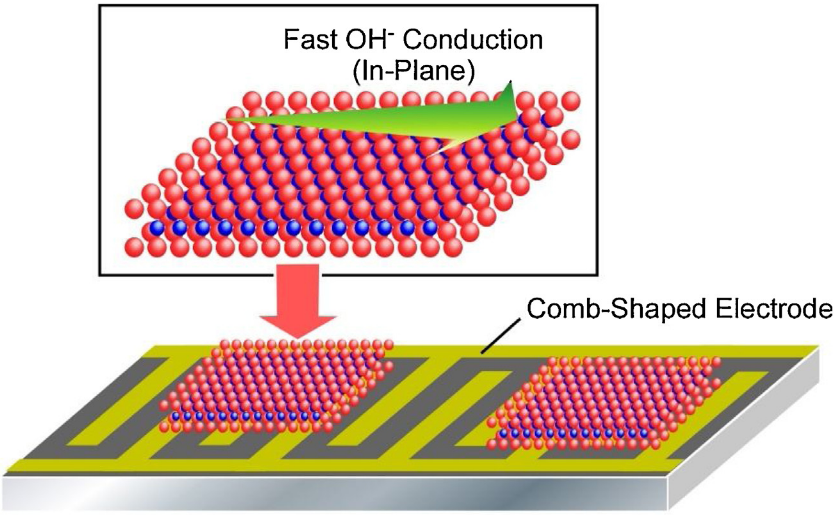


Fig. 17. A single layer nanosheet of layered double hydroxide with exceptionally high hydroxyl ion conductivity with its highly anisotropic nature that were tested on comb-shaped electrodes.

version efficiency. The synthesized fused bithiophene-imide-based polymer can be regarded as a promising *n*-type polymer for various device applications.

Chemical nanoarchitectonics on conjugated polymers with multi-step cleavage capability of side chains can lead to facile production in printed organic electronics through adjustable processability. Processes with water for fabrication of functional polymers such as conjugated polymers are advantageous in cost suppression, environmental-risk minimisation, and scaling up printing processes. For such target, Reynolds and co-workers synthesized polythiophene-based conjugated polymers with multi-step cleavable side chain (Fig. 14) [138]. The initial form is soluble in organic solvents with high advantages in compound purification, and the first cleavage of the side chain from ester to carboxylate converts its organic-solvent-soluble nature to water-soluble one. Water-based printing process becomes possible with this second form. The second cleavage results in removing unnecessary parts from conjugated polymers to produce target

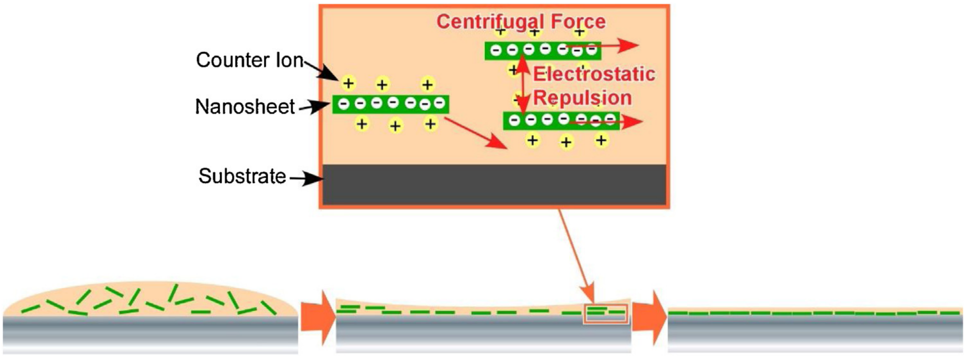


Fig. 18. A method to synthesize defect-less monolayer of two-dimensional materials within a process time of 1 min without forming edge overlapping by centrifugal force.

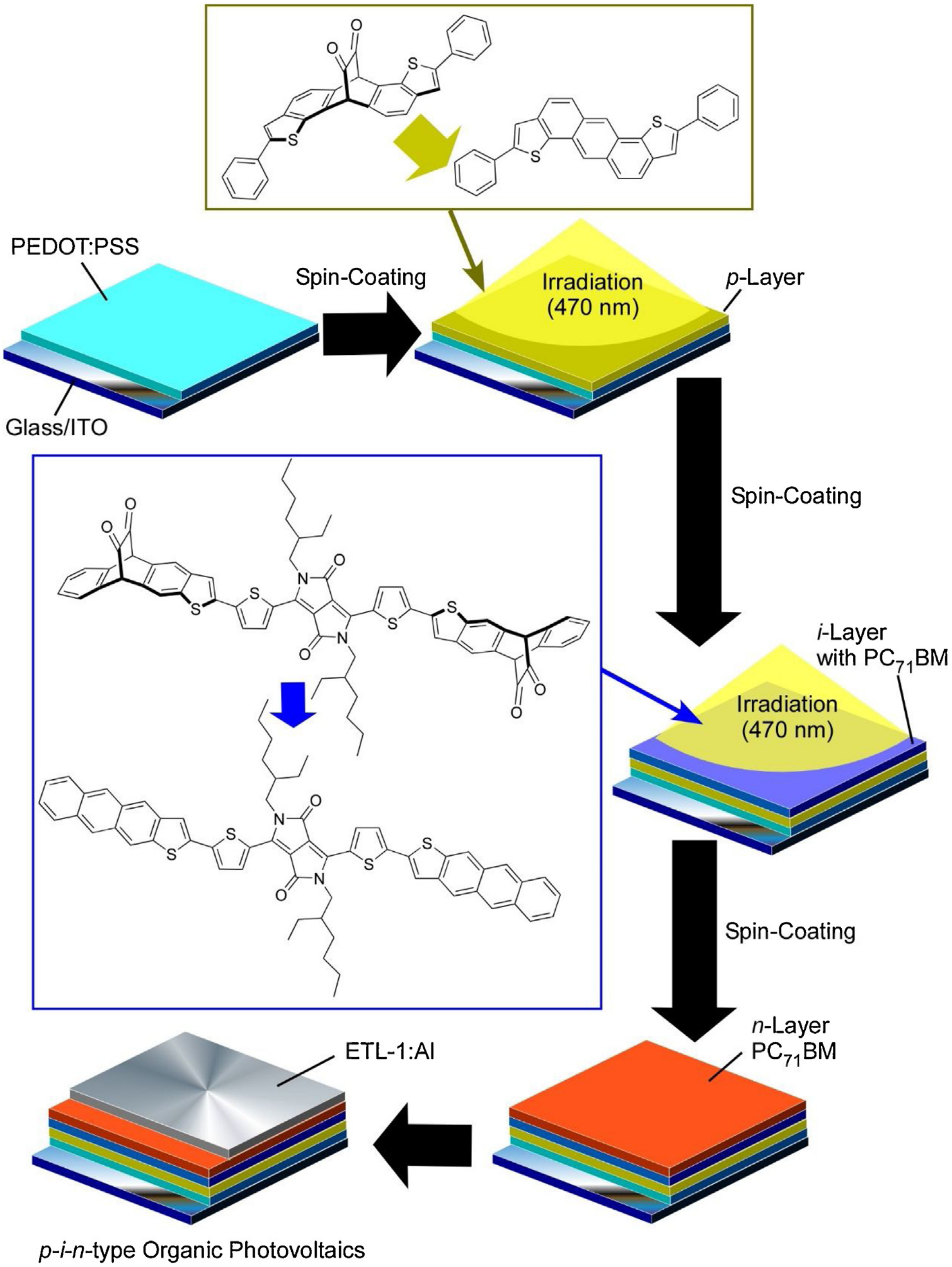


Fig. 19. A photochemical layer-by-layer solution process that can place right material at the right position in organic semiconducting thin films of ternary photovoltaic device structures. The fabricated *p-i-n*-type organic photovoltaic device (i-layer represents intermixed layer) exhibited a one-order higher efficiency than the corresponding bulk-heterojunction device. PEDOT:PSS (poly(3,4-ethylenedioxythiophene):polystyrene sulfonate) and $PC_{71}BM$ ([6,6]-Phenyl-C71-butyric acid methyl ester) were used.

electronic materials with solvent-resistant capability. This stepwise chemical nanoarchitectonics process would be advantageous for fabrication of organic field-effect transistors, electochromic devices, organic photovoltaics, and bio-conjugated devices.

Nanoarchitechtures in polymer/small molecule hybrid play a decisive role for functionalizing optoelectronic devices. Iodine-doped polyacetylene [139] and bulkheterojunction solar cell consisting of semiconducting polymer and fullerene derivative [140] are the most representative hybrid material. A soft polymeric media can permit small molecules to intercalate into their free volume. The resulting unique host-guest hybrid nanostructure between polymer network and small molecule has been of great interest particularly in electronic devices, where hybridization factors such as dipole interaction and charge transfer interaction at physical/chemical contacts, are likely to modulate device performance. Most recently, Kang, Watanabe, Sirringhaus and co-workers have demonstrated two-dimensionally ordered polymer/small molecule nanostructure simple by thermally depositing a guest acceptor molecule on the top of polythiopehene-based semiconducting polyemer [141,142]. The introduced guest acceptor is found to diffuse into the entire bulk of polymer network and reside particularly within the layer of side chains (Fig. 15). Surprisingly, the incorporation of the guest dopant molecules into the side-chain regions even enhances the structural order in the polymer backbone. In this highly-ordered donor-acceptor hybrid system, not hopping, but coherent charge transport properties are confirmed comprehensively by observing an ideal Hall effect. Hybridizing multiple organic composites into highly ordered nanoarchitecture can open opportunities to new functionalities that are not accessible only by a single component of organic material.

Nanoarchitectonics for devices with inorganic nanomaterials

Unlike organic molecules, inorganic materials have limited structural flexibility. However, inorganic materials often exhibit well-defined and discrete properties depending on their sizes, anisotropic natures, structures, orientation, and arrangements. Because these characteristics of inorganic materials are advantageous for reliable performances of devices, nanoarchitectonics efforts with inorganic nanomaterials have important contributions to device technology. In addition, various unexplored functions and phenomena remains in inorganic nanomaterials science although observations and evaluation of inorganic materials in nanometer scales might be more advanced than those for organic materials with certain fluctuations. For example, as discovery of novel physical phenomenon, Uchida et al. have found recently an anisotropic magneto-Peltier effect. In this phenomenon, the Peltier coefficient can be altered though changing the angle between the directions of a charge current and magnetization in a ferromagnet [143]. Komatsu, Moriyama, and co-workers reported observation the quantum valley Hall state in the ballistic aligned superlattices of graphene and hexagonal boron nitride [144]. It was achieved one-dimensional edge contacts of these two-dimensional nanomaterials as materials nanoarchitectonics. Nanoarchitectonics on inorganic materials would activate such unexplored discovery as well as sophistication of device technology.

Recent attractive inorganic materials are two-dimensional materials that have been used for a wide range of applications including energy application, device technology, and even biomedical usage. One of the most promising two-dimensional material, molybdenum disulfide (MoS_2) nanosheet, is used for field-effect transistors, because MoS_2 nanosheet has excellent electrical and optical properties. Although MoS_2 nanosheets are usually synthesized by chemical vapour deposition, fabrication methods of MoS_2 nanosheets compatible with currently developing solution processes for channel materials become important. Lee and co-workers reported synthesis of single-layer edge-1 T basal-2H MoS_2 nanosheet together with application to field-effect thin film transistor [145]. Modification of MoS_2 upon nucleophile-electrophile chemical reaction using 4-carboxy-benzenediazonium results in edge-functionalization of MoS_2 materials COOH groups and facilitates exfoliation. The resulting single-layer edge-1 T basal-2H MoS_2

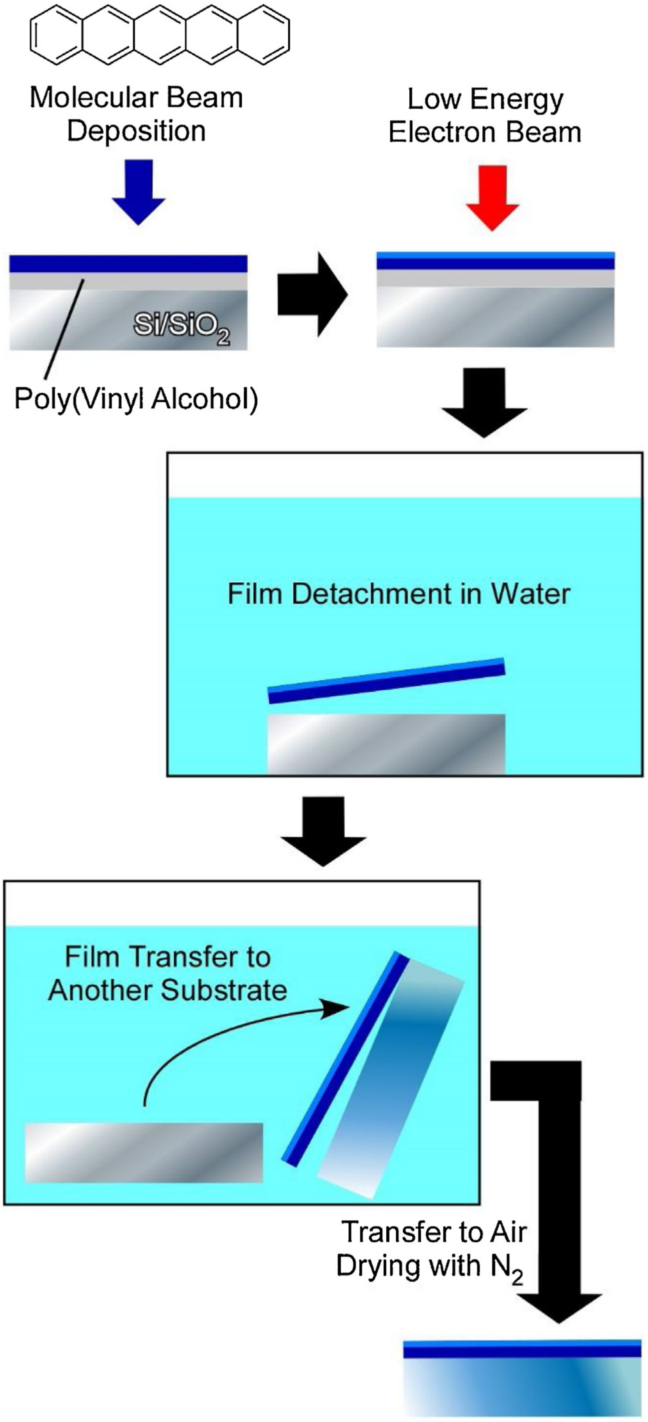


Fig. 20. Transfer of an organic semiconductor nanosheet onto another substrtate for electronic device applications in which irradiation of the electron beam crosslink the topmost layer (ca. 5 nm corresponding to 3–4 monolayers) of original pentacene films in ca. 50 nm of thickness with keeping pristine crystallinity.

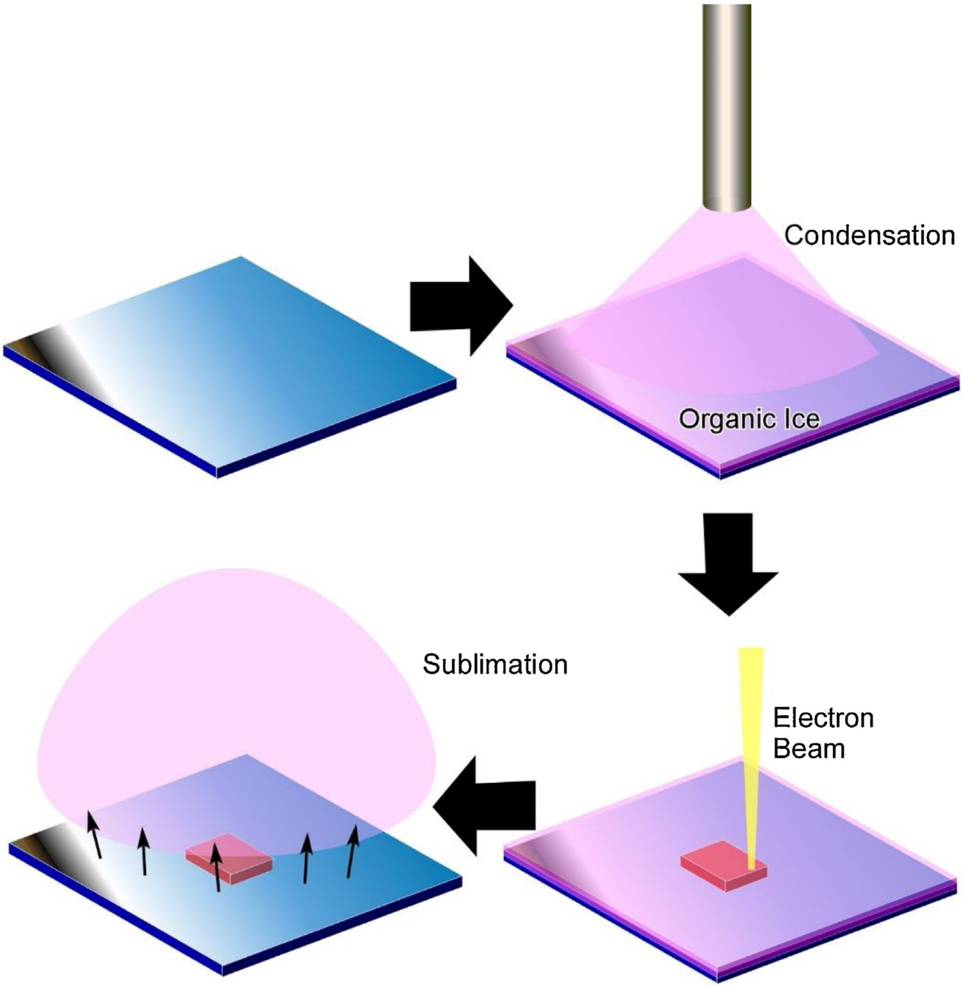


Fig. 21. An electron-beam lithography using organic ice resists for patterning of device preparation using simple organic molecules such as alcohols as resist materials, which are condensed on the substrates, reacted with electron beams, and removed from the substrate via sublimation.

nanosheets were then fabricated through cross-linking with the aid of a cationic polyelectrolyte, polydiallyldimethylammonium chloride, to form good-quality films for a channel of the solution processing thin-film transistor. The fabricated thin film transistor showed very high mobility. Chemical nanoarchitectonics of this edge functionalization can be used for various two-dimensional bulk inorganic materials to functionalize two-dimensional materials for electronic devices with low cost processes.

Nanoarchitectonics of complex perovskite oxides is an attractive research target to produce functional materials through regulation of various electronic and magnetic characteristics including high-temperature superconductivity, high-κ ferroelectricity, and quantum magnetism. Osada and co-workers successfully prepared two-dimensional perovskites with high-κ ferroelectricity through nanoarchitectonic atomic layer engineering using perovskite nanosheets ($Ca_2Na_{m-3}Nb_mO_{3m+1}$; $m = 3–6$) (Fig. 16) [146]. Nano-fims of this homogeneous two-dimensional perovskite nanosheets were fabricated in assembling manner of unit-cell-by-unit-cell. Thickness precision of the perovskite nanofilms becomes ca. 0.4 nm, i.e., a single perovskite layer with enhanced high-κ dielectric response. This kind of exploration on high-κ dielectric two-dimensional materials would have great contributions to electronic devices such as capacitors, memories, and gate devices as well as post-graphene technology.

Supplying good performance materials with controlled nanostructures to fuel cell technology is a crucial matter in energy strategies in these days. Current technology on fuel cells is mostly based on proton conductors. However, this situation limits precious metals such as Pt as an electrocatalyst because of required low pH conditions for operation. If conducting ion is replaced by hydroxyl ion, a wide range of cheap metals can be used as electrocatalysts under high pH conditions. Unfortunately, conductivity of conventional hydroxyl ion conductors is much less than that for well-used proton conductors such as Nafion. Recently, Ma, Zhu, and co-workers successful prepared single layer nanosheet of layered double hydroxide having exceptionally high hydroxyl ion conductivity with its highly anisotropic nature (Fig. 17) [147]. Upon exfoliation nanoarchitectonics to create ultimate two-dimensional nanosheet from layered double hydroxide crystals, the morphological and structural anisotropy resulted in high conductive anisotropy. Enhanced adsorption of water on the surface of single layer layered double hydroxide nanosheet increases mobility of hydroxyl ions. Maximized in-plane conduction of hydroxyl ions of two-dimensionally nanoarchitected layered double hydroxide would lead to high performance fuel cell devices operative under basic conditions.

Nanoarchitectonics processes for device preparation

Methods to fabricate functional device structures from nanoscale units are important items in nanoarchitectonics. In addition to various fabrication technologies, self-assembly based on

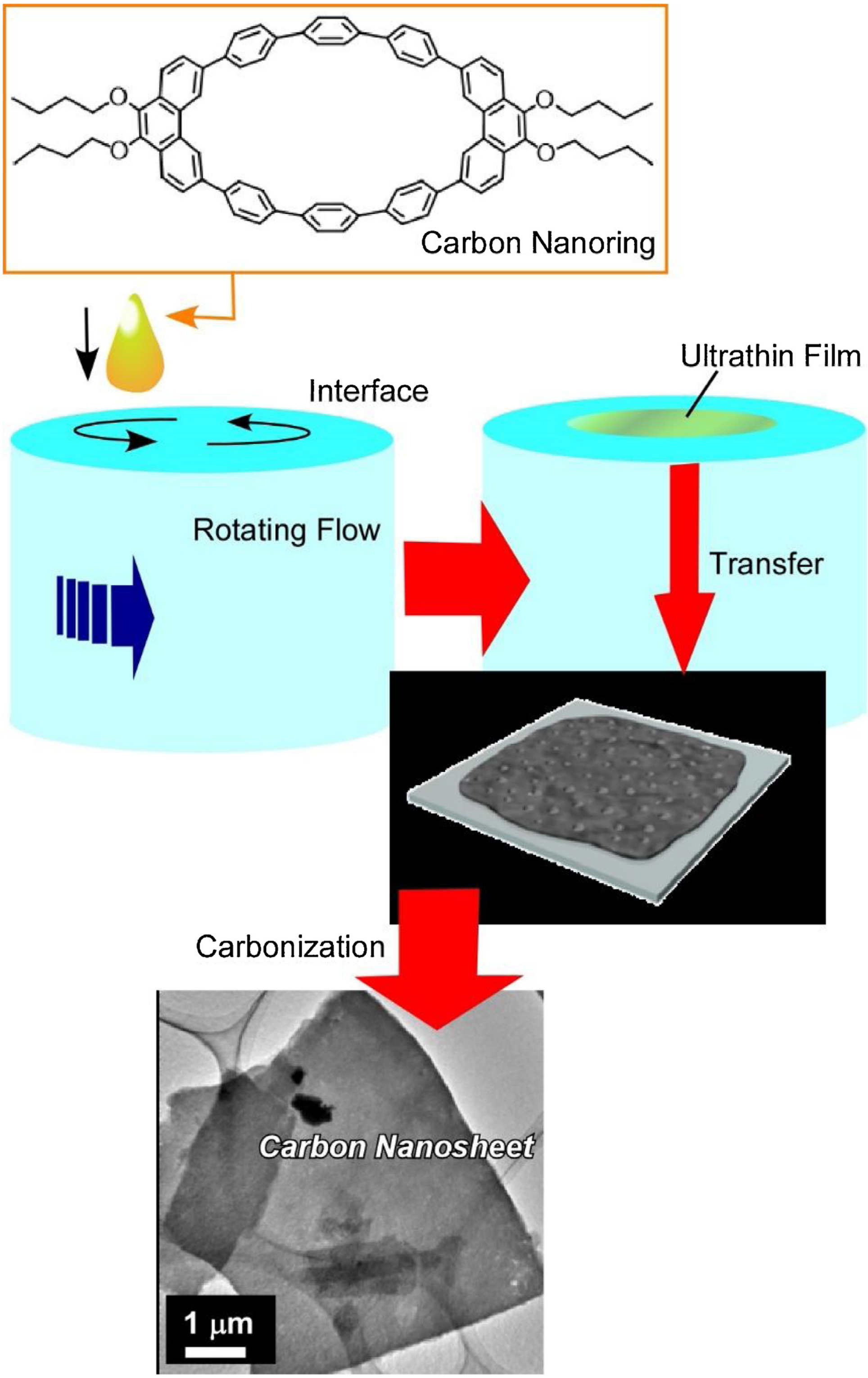


Fig. 22. A vortex Langmuir-Blodgett (vortex-LB) method and morphology-retained carbonization to fabricate a carbon nanosheet from carbon nanoring molecules.

specific molecular interactions and thin film fabrication methods including self-assembled monolayer (SAM) method [148,149], Langmuir-Blodgett (LB) technique [150–152], and layer-by-layer (LbL) assembly [153–157] are often used. These strategies basically provides defined sidle layer structures, multi-layered structures with high organization, and multi-layered structures with flexible natures, respectively. Each of them have their own limitations in fabrication speeds and applicable materials. However, modification of these methods can overcome these limitations. As described below, in recent research, their modified techniques and novel methods have been also explored. They often provide advanced features in fabrications of devices.

For example, Matsuba, Wang, and co-workers proposed method to synthesize defect-less monolayer of two-dimensional materials within a process time of 1 min (Fig. 18) [158]. Their method is based on so-called spin-coating method to provide dense mono-

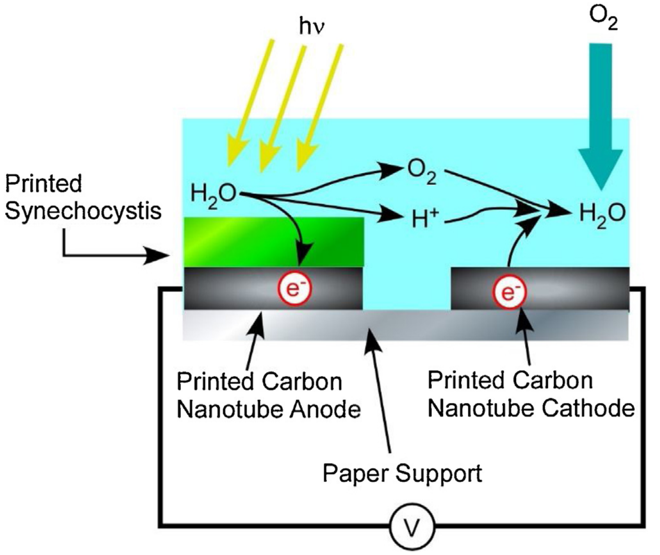
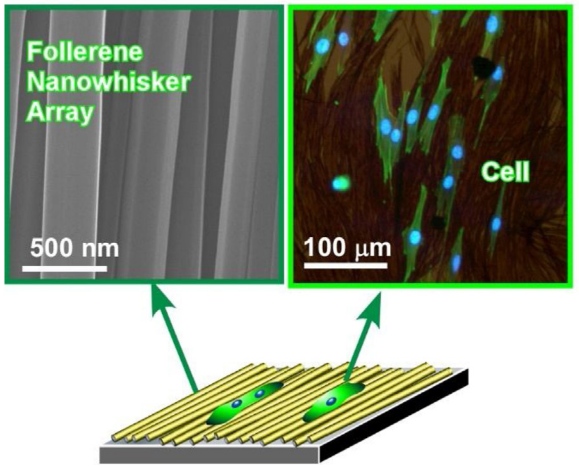


Fig. 23. Amicrobial biophotovoltaic cell where cyanobacteria and microalgae are utilized for conversion of light energy to electrical current using water as the source of electrons.

(A) On Surface of Aligned Nanocarbon Assembly



(B) At Interface between Water and Fluorocarbon

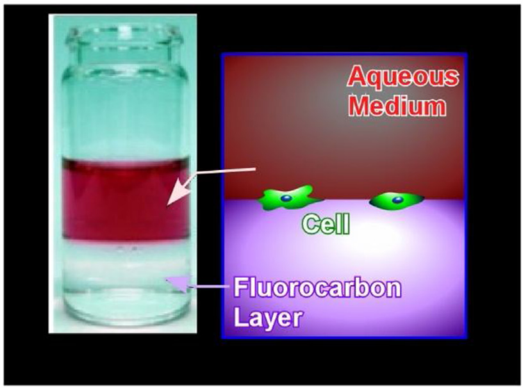


Fig. 24. Cell cultures and regulation of cell differentiations: (a) on surface of aligned fullerene nanowhiskers; (B) at interface between aqueous medium and fluorocarbon solvent.

layer through tiling of two-dimensional materials such as graphene and metal oxide nanosheets from their precursor fluidic samples such as dimethyl sulfoxide suspension. The main process is usually completed within 1 min and provides a uniform film over large area (for example, 30-mmφ substrate). The nanosheets can be assembled as closely packed tiles without forming edge overlapping by centrifugal force. In addition, repeated operation of this process resulted in formation of multilayer structures as high quality two-dimensional films. Higher quality films can be obtained by optimization of preparative conditions including precursor concentration and rotation speeds together with heat treatments at moderate temperature.

Nanoarchitectonics to efficiently bridge functions between different materials in active layers is important for optimization of performance in organic devices. Suzuki et al. proposed a novel photochemical layer-by-layer solution process that can place right material at the right position in organic semiconducting thin films of ternary photovoltaic device structures (Fig. 19) [159]. This method can nanoarchitect various organic semiconducting materials including wide-band-gap small molecules and narrow-band-gap π-extended materials into rational structures. In their approach, α-diketone derivatives of acenes are used as photoreactive precursors that have higher solubility for processing than the corresponding acenes. The precurcers were converted into insoluble acenes through decarbonylative aromatization by visible right irradiation. The fabricated *p-i-n*-type organic photovoltaic device (i-layer represents intermixed layer) exhibited a one-order higher efficiency than the corresponding bulk-heterojunction device, because internal quantum efficiencies becomes much higher. This method can be generalized to various layer-structure-based organic devices.

Unlike two-dimensional inorganic materials such as graphene with covalent bonded atom networks, films of organic semiconductors assembled with van der Waals interactions are not tolerant toward conventional peeling-off and transfer procedures. Therefore, device preparation with organic semiconductors have certain limitations. Turchanin, Nickel, and co-workers demonstrated ways of synthesis of transferable organic semiconductor nanosheets for electronic device applications (Fig. 20) [160]. The proposed nanoarchitectonic strategy is based on crosslinking of external layers of organic semiconductor films by irradiation of low energy electron beam. Detachment of the crosslinked layer from original substrate and subsequent deposition onto another substrate without serious disturbances of structural natures become possible with this strategy. For example, irradiation of the electron beam crosslinks the topmost layer (ca. 5 nm corresponding to 3–4 monolayers) of original pentacene films in ca. 50 nm of thickness with keeping pristine crystallinity. Charge injection properties of the transferred layers in the field effect transistors was confirmed to be superior to that for over pentacene films grown by vapour deposition. The proposed methodology is useful for devices with hybrid structures and unusual geometries as well as use of substrates unfavourable for direct growth process.

Han and co-workers demonstrated a novel electron-beam lithography using organic ice resists for nanoarchitectonic patterning of device preparation (Fig. 21) [161]. Their method uses simple organic molecules such as alcohols as resist materials, which are condensed on the substrates, reacted with electron beams, and removed from the substrate via sublimation. Irradiation of electron beams alters molecules to non-volatile solid products with very local area. Lithographic performances depend highly on used organic compounds (1-pentanol, methoxybenzene (anisole), nonane, and isopropanol). The compound with lowest vapour pressure (1-pentanol) showed lowest deposition rates resulting in uniform ultrathin layers (7 nm). In contrast,

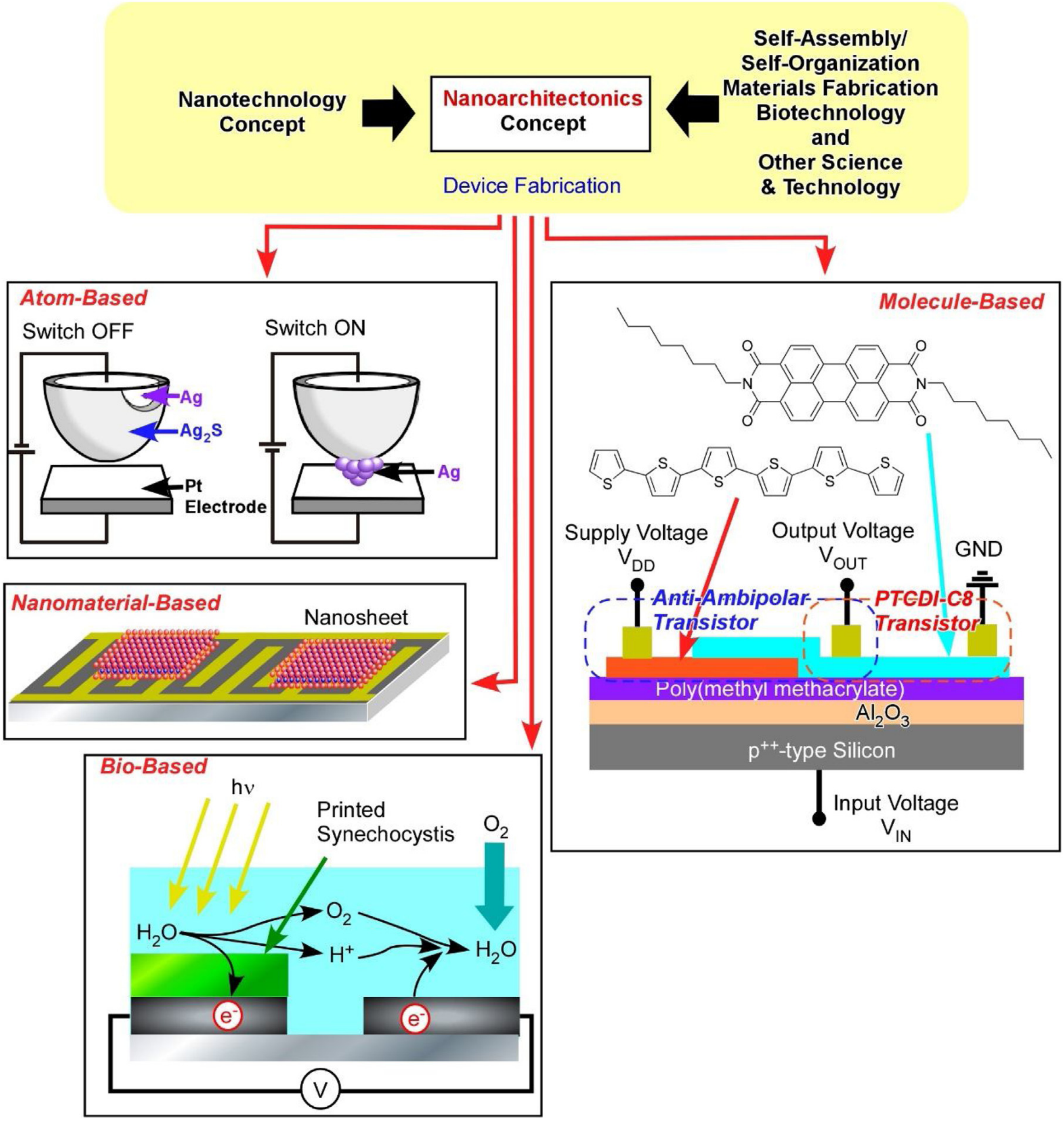


Fig. 25. Nanoarchitectonics with various design of fabrications on advanced devices and related functional systems using atoms, organic molecules, nanomaterials, and bio-stuffs.

patterning using isopropanol with lowest freezing point cannot give well-reproducible results. When ethoxybenzene, (anisole) and nonane ices were used for resists, ideal films for lithography applications with thickness of 20 to 200 nm were readily formed. This method has several advantageous features as compared with conventional electron beam lithography. Only a single instrument without cleanrooms-like facilities are only required because chemical exposures to workers are supressed in the lithography using organic ice resists. In this method, patterning on fragile membranes only thickness of 5 nm is possible. Pattern sizes from nanometer to sub-millimeter scale can be prepared as well as three-dimensional motifs fabricated upon stacking layers of frozen organic molecules.

Nanocarbons and two-dimensional materials are important items in current device technologies such as energy storage devices. As emerging nanoarchitectonics approaches, bottom-up syntheses of such functional nanomaterials from well-designed organic molecules have been paid attention. Recently, Mori et al. reported successful synthesis of carbon nanosheets from designed carbon nanoring (9,9′,10,10′-tetra-butoxy-cyclo [6]-paraphenylene-[2]-3,6-phenanthrenylene) by novel technique, so-called, vortex Langmuir-Blodgett (vortex-LB) method with morphology-retained carbonization (Fig. 22) [162]. The carbon nanoring molecules with ellipsoidal shape were easily assembled into two-dimensional film on vortex flow at the air-water interface. The chloroform solution of the carbon nanoring molecules was first spread on water surface under the vortex flow. The resulting film was kept for short time to evaporate the remaining solvents after the vortex motion was stopped. Transferred thin film onto a solid substrate has thickness of ca. 10 nm, corresponding to stacking of five molecular layers in the tandem nanostructure. Evaporation of trapped solvents created mesoporous nanostructure well-dispersed on two-dimensional plane. The obtained films were then carbonized at 850 °C for 3 h under nitrogen gas flow to results in large-scale carbon nanosheets with the almost identical thickness. Although conductivity of the film before carbonization is negligible, sufficiently high conduc-

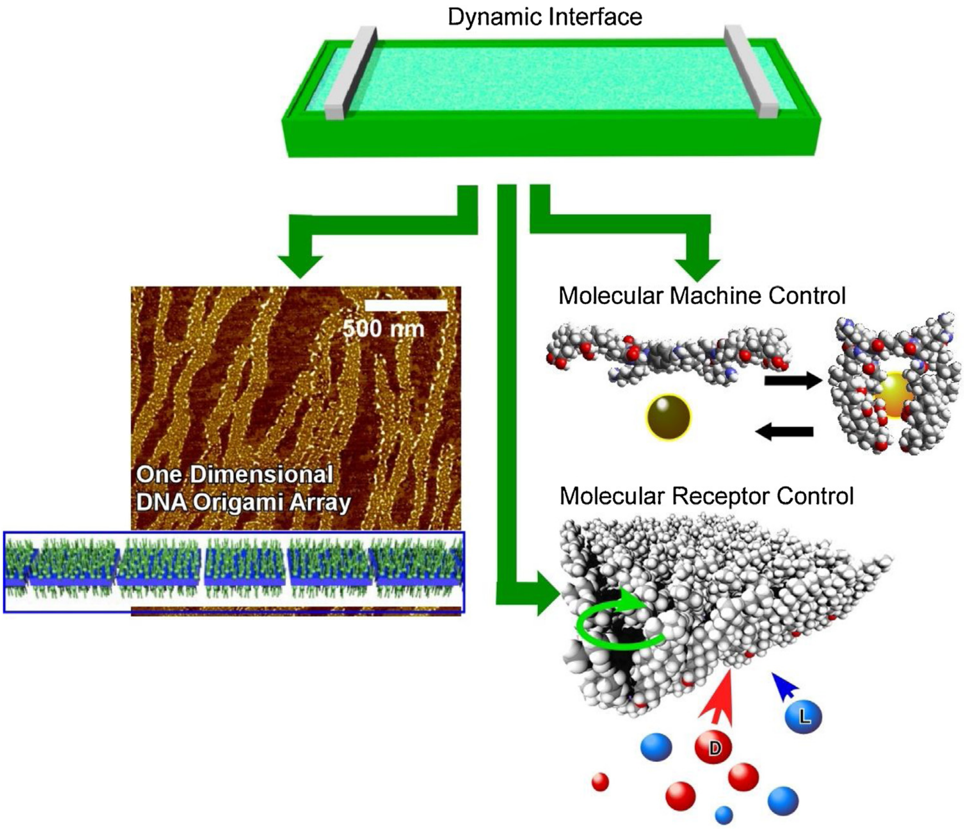


Fig. 26. New challenges on dynamic nanoarchitectonics at the air-water interface: intentional alignment of DNA origami pieces into one-dimensional wire structures and controls of molecular machines and molecular receptors.

tivity (1.98×10^3 S m^{-1}) was confirmed for the carbonized film. This fact suggests graphitization of the carbonized films. Mixing of pyridine molecules at the vortex-LB process and subsequent carbonization provided the similar carbon nanosheets with N-doped nature. The N-doping procedure further increased film conductivity. The obtained N-doped carbon nanosheets are expected to work as a highly efficient catalyst on oxygen-reduction reactions fuel cell devices.

Challenge to device-bio conjugation

From the following two viewpoints, inclusion of bio-based consideration into device technology is crucial. One reason is use of devices in biological media and life active environment. In these cases, bio-based considerations such as bio-friendly nature and bio-compatibility become crucial factors for device design. For example, biocompatible energy storage systems are necessary to power electronic medical implants and sensors in biological usages as summarized in a recent review article by Stauss and Honma [163]. Toxic materials commonly used in batteries have to be encapsulated in bio-related uses. However, battery design for batteries using biocompatible electrodes and electrolytes can overcome such limitations. Not limited to powering batteries, efforts to make device biocompatible would drastically expand possibilities of usages of robots, drones, and environmental sensing systems.

Another motivation is use of high functions of biomolecules as parts of device components. High efficiency and selectivity in molecular/energy conversions and signal transductions in biological systems are often exceed those in man-made devices. Therefore, inclusion of functional biomolecules into device structures may make sufficient progresses in device functions [164–167]. In the later cases, bio-based considerations on facile conjugation between bio-components and artificial devices are important factors for device fabrications. Not limited to such advanced device systems, biomedical devices in current real uses require engineering development on interfaces between ionic biosystems and electric devices as suggested by Nishizawa in his recent article entitled soft, wet and ionic microelectrode systems [168]. As compared with dry fabrication processes in conventional devices, wet processes for biomaterials such as polymers, hydrogels, DNA, proteins, and cells have not been fully explored, because these processes require physiologically mild conditions. This research group explores interfacing wet ionic systems and dry electronic systems using carbon-nanotube-modified electrodes and conducting polymer-based electrodes. These systems possess both large surface capacitance and high affinities with bio-systems. Dense immobilization of enzymes and stimulation of cells and tissues are possible. Furthermore, carbon-nanotube-based enzyme electrodes for build-in biofuel cells enables self-powered sensors in biological environment and skin patches.

Nixon and co-workers demonstrated fabrication of microbial biophotovoltaic cells where cyanobacteria and microalgae were utilized for conversion of light energy to electrical current using water as the source of electrons [169]. Nanoarchitectonic fabrications of the bio-photovoltaic device relies on conventional ink-jet technologies. On top of a carbon nanotube conducting surface, biophotovoltaic devices with a layer of cyanobacterial cells were fabricated with commercial inkjet printer. Because printing processes with bio-ink of cyanobacterial cells on paper substrate are done under mild conditions, printed cells were fully viable. The immobilized cyanobacteria cells can generate electrical currents both in respond to light as a bio-solar-panel and in the dark as a solar bio-battery. Functions of the fully printed biophotovoltaic device (Fig. 23) was demonstrated. This system has advantages over conventional microbial fuel cells with requirements of organic carbons for microbial growth. In addition, this method is available to immobilize biomolecules such as enzymes and DNA and to significant scaling up for industrial applications. Therefore, practical uses such as bioenergy wall papers can be expected.

Living cells have much potential to be living devices with multiple functions because they have excellent stimuli-responsive properties. For future cell-based bio-device nanoarchitectonics, intentional immobilization, organization and differentiation of living cells at interfacial medium becomes crucial. Several efforts on cell cultures and regulation of cell differentiations on nanostructured surfaces have been made [170,171]. Some examples are shown in Fig. 24. At surfaces of aligned fullerene nanowhiskers with sufficiently hard mechanical nature, bone forming human osteoblast MG63 cells aligned and extended to direction of the nanowhisker alignment [172]. This method would provide highly anisotropic arrangements of functional cells on device surfaces. The C2C12 myoblast cells cultured on the aligned fullerene nanowhiskers exhibited significant enhancement of myogenic differentiation and regulated the direction of myotube formation [173]. Not only cell alignments but also cell differentiations can be regulated at aligned nanostructures formed on a solid support. In contrast, C2C12 myoblast cells cultured at liquid-liquid interface, interface between aqueous medium and fluorocarbon solvent, altered situation of cell differentiation significantly [174]. At this extremely soft interfaces, significant attenuation on expression of myogenic regulatory factors family gene was observed. Fluidic micro-environmental nature of culture medium greatly affects regulation of myogenic differentiation. Detailed research with human mesenchymal stem cells similarly at the interface between an aqueous culture medium and a perfluorocarbon fluid layer revealed the important roles of monomolecular protein nanosheets spontaneously formed at the culture process [175]. Packing of proteins in these nanosheets can be finely tuned depending on structures of used fluorocarbon liquids, which modulate mechanics of the protein layers and the resulting cell spreading. These biofilms with protein and cells can be transferred in a solid surface by Langmuir-Blodgett and related methods. Therefore, these interfacial methods can nanoarchitect cells with intentional regulation of alignment, spreading, and differentiation on a solid surface, which opens new avenues for bio-device fabrications.

It has to be noted that biomolecules such as enzymes are capable of being controlled by single atom or ion. Therefore, nanoarchitectonics arrangements of biomolecules can be coupled with atom/molecular-level nanoarchitectonics to create bio-function-conjugated devices. Conjugation is not limited to covalent linkages, non-covalent assemblies of biomolecules and functional molecules at membrane media would accomplish bio-chemistry conjugated devices [176,177]. Recently, Li and wisely conjugated photosensitive proton release molecular functions and ATP production by ATPase on lipid membranes to construct photo-ATP converting systems [178]. In addition, efforts by molecular-level nanoarchitectonics for device fabrications have been continuously reported [179–181]. These functional molecular units can be potentially integrated in bio-functional systems.

Summary and perspectives: dynamic nanoarchitectonics at interface

In this review article, various designs of fabrications on advanced devices and related functional systems are exemplified basically according to classification of key operation materials, atoms, molecules, polymers, inorganic stuffs, and biomaterials (Fig. 25). As seen in two-dimensional-crystal-based organic semiconductor devices, precise design and organization of key components are crucially important for optimization of device performances. In these cases, molecular designing optimized for avoiding unfavorable molecular disturbance and defect-free two-dimensional organization results in enhanced performances of devices. Precise nanoarchitectonics with rational construction of functional devise structures from molecular bottoms are required. Emerging method to fabricate high quality structures can contribute to these demands. In contrast to the above-mentioned case, some device performances utilize dynamic motions and properties of key components as seen in synapse-like atomic switches, decision-making nanoionic devices, stimuli-responsive polymer-based devices, and bio-integrated devices. Keys of functions of these devices rely on dynamic motion, diffusion, conformational modifications, and arrangement changes. The latter features are much different from conventional device designed with static and precise positioning of functional components. Therefore, inclusion of dynamism spices into well-fabricated traditional device configurations is important factor for future advanced devices.

Such device-like functional structures can be commonly seen in biological systems where many functional units such as proteins and pigments are working together with significant dynamisms. In addition, such dynamic systems in biological systems are often confined at interfacial environments such as cell membranes. These features can be imported to man-made device systems though regulation of dynamic functions at interfacial media. We already exemplified several systems on controls of dynamic nanoarchitectonics at the air-water interface as a model interfacial media (Fig. 26) [182–186]. For example, intentional alignment of DNA origami pieces into one-dimensional wire structures [187], reversible capturing external molecules [188,189], tuning of molecular receptors for best sensing performances [190,191], and regulations of various motions of molecular machines [192–195] are actually demonstrated on the basis of dynamic molecular motions. Such dynamism of functions at interfaces would be incorporated into device structures as two-dimensional soft devices. In such case, necessary factors, precise control of nano/microstructures and allowance of dynamic or even ambiguous motions of the devise components, are actually conflict each other but have to be merged and balanced. This difficult problem can be solved by the nanoarchitectonics concept that aims to construct functional systems with nanoscale precision allowing various uncertainties.

Acknowledgements

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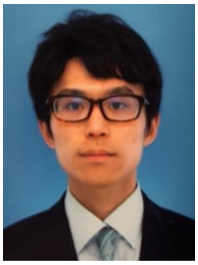

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