

Layer-by-Layer Assembly: Recent Progress from Layered Assemblies to Layered Nanoarchitectonics

Katsuhiko Ariga,^{*,[a, b]} Eungjin Ahn,^[c] Minju Park,^[c, d] and Byeong-Su Kim^{*,[c]}



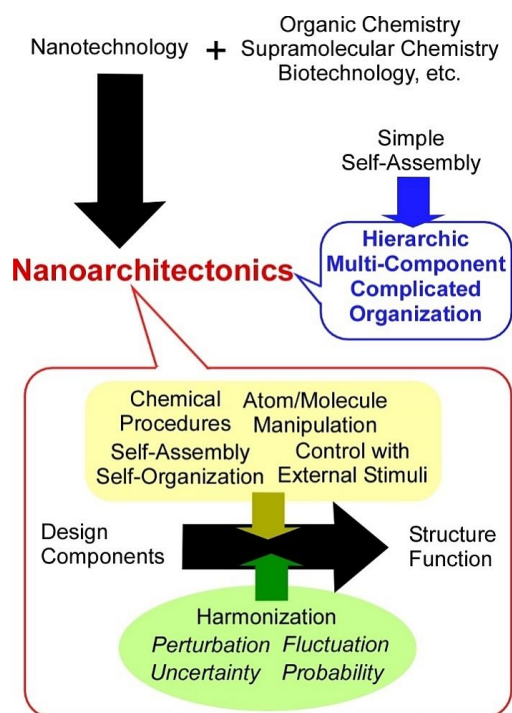
Abstract: As an emerging concept for the development of new materials with nanoscale features, nanoarchitectonics has received significant recent attention. Among the various approaches that have been developed in this area, the fixed-direction construction of functional materials, such as layered fabrication, offers a helpful starting point to demonstrate the huge potential of nanoarchitectonics. In particular, the combination of nanoarchitectonics with layer-by-layer (LbL) assembly and a large degree of freedom in component availability and technical applicability would offer significant

benefits to the fabrication of functional materials. In this Minireview, recent progress in LbL assembly is briefly summarized. After introducing the basics of LbL assembly, recent advances in LbL research are discussed, categorized according to physical, chemical, and biological innovations, along with the fabrication of hierarchical structures. Examples of LbL assemblies with graphene oxide are also described to demonstrate the broad applicability of LbL assembly, even with a fixed material.

1. Introduction

Considerable scientific and technological effort has been invested to meet the global need for environmentally friendly, emissionless, and pollutionless processes, including the development of molecular/material syntheses,^[1] the fabrication of new systems/devices/sensors,^[2] and advancements in energy production/management^[3] and biological/biomedical treatments.^[4] Vital to these efforts has been the precise control of the component structures and organization at the nanoscale level,^[5] to enable the efficient flow and conversion of materials, signals, and energy.^[6] Recently, we have seen rapid technological developments in the observation and fabrication of nanoscale objects,^[7] in a field known as “nanotechnology”.^[8] To enable further advancements in this area, Aono and co-workers first proposed the concept of “nanoarchitectonics”, which is a new concept for the fabrication of functional material systems by using nanoscale unit components.^[9,10]

The nanoarchitectonics concept develops nanotechnology as a materials-production strategy by combining it with other scientific fields, such as organic chemistry, supramolecular chemistry, and biotechnology (Scheme 1).^[11] Besides self-as-



Scheme 1. Outline of the nanoarchitectonics concept: a fusion of nanotechnology and the other research fields, the harmonization of various actions, and the conversion of simple self-assembly into hierarchical structures.

sembly processes, nanoarchitectonics can include chemical synthesis, atom/molecule manipulation, chemical nanomanipulation, and field-induced material control. Because certain uncertainties based on thermodynamic perturbations, statistical uncertainties, and quantum effects are unavoidable on the nanoscale, harmonization of the interactions and effects is particularly important in nanoarchitectonics processes.^[12] The nanoarchitectonics approach can be advantageous for the preparation of complicated and hierarchical structures from multiple components, compared to precise nanofabrication and self-assembly from single or a few components.^[13] Although nanoarchitectonics is still an emerging concept, its potential for the construction of functional systems from a variety of components has been proposed for a wide range of research fields, including materials production,^[14] structure organization,^[15] sensors,^[16] environmental applications,^[17] cataly-

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

[b] Prof. Dr. K. Ariga
Graduate School of Frontier Sciences
The University of Tokyo
5-1-5 Kashiwanoha, Kashiwa
Chiba Prefecture 277-8561 (Japan)

[c] Dr. E. Ahn, M. Park, Prof. Dr. B.-S. Kim
Department of Chemistry
Yonsei University
Seoul 03722 (Republic of Korea)
E-mail: bskim19@yonsei.ac.kr

[d] M. Park
Department of Chemical Engineering
Ulsan National Institute of Science and Technology (UNIST)
Ulsan 44919 (Republic of Korea)

ⓑ The ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/asia.201900627>.

sis,^[18] energy production,^[19] device applications,^[20] and biological/biomedical usages.^[21]

However, the construction of functional architectures in all three dimensions is not always easy. Thus, the direction-fixed construction of functional materials, such as layer-by-layer nanoarchitectonics with various components, is a realistic starting point for demonstrating nanoarchitectonics. Compared to the various fabrication techniques that have been developed for thin films and layered structures, including the Langmuir–Blodgett (LB) method,^[22] layer-by-layer (LbL) assembly offers a high level of freedom in its component applicability and technical availability. The LbL-assembly approach bears some nanoarchitectonics aspects,^[23] although the LbL technology first appeared much earlier than the nanoarchitectonics concept.^[24] Therefore, a review of recent progress in LbL assembly would be a nice guide to help learn the current state of the field and the expected future directions of nanoarchitectonics research.

This Minireview summarizes the recent progress (especially in the 21st century) in the science and technology of LbL assembly. After briefly explaining the fundamentals of the LbL approach, recent research into LbL assembly is introduced, with a focus on physical, chemical, and biological innovations, together with the fabrication of hierarchical structures, such as layered superlattices and nanoarchitectures. In the following section, focused examples on LbL assemblies that employ graphene oxide (GO) nanosheets are described to show the wide applicability and availability of LbL assemblies with recent materials of interest. These recent advancements in LbL assembly demonstrate the development of LbL technology from layered assembly to layered nanoarchitectonics.

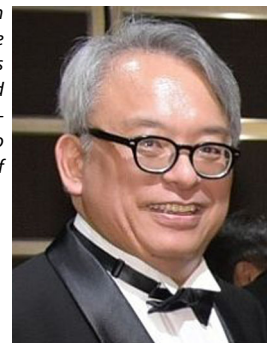
2. Fundamentals of LbL Assembly

Before we summarize recent progress in LbL assembly, we will begin by briefly introducing the fundamentals of the LbL technique. Following a conceptual proposal on the LbL assembly of charged colloidal particles by Iler,^[25] Decher et al. demonstrated LbL assembly by using polyelectrolytes and charged bolaamphiphiles (polyelectrolyte/polyelectrolyte and polyelectrolyte/bolaamphiphile assemblies).^[26] In parallel, a layered assembly based on zirconium–phosphate interactions was demonstrated by Mallouk and co-workers.^[27] Following these pioneering research accomplishments, the applicability of the LbL concept was demonstrated for a wide range of materials, such as conventional and functional polymers,^[28] inorganic materials,^[29] biomaterials,^[30] viruses,^[31] other nanomaterials,^[32] and molecular assemblies.^[33]

LbL assemblies exhibits the distinctive features of simplicity and inexpensive procedures.^[34] Multilayer nanoarchitectures can be obtained on a solid substrate by simply dipping the substrate into solutions of the target components (Scheme 2A). Fabrication processes can be performed with just beakers and tweezers, with an adsorption step of approximately 10 min. In LbL-assembly methods in which electrostatic interactions act as the driving force for assembly, charge neutralization and resaturation upon the adsorption of counterionic component materials onto a charged surface result in charge

inversion, which enables the alternate adsorption of cationic and anionic species as nanofilms. The numbers of layers and layer sequences can be desirably modified by changing the sequence of the adsorption processes. The driving force for LbL assembly is not limited to electrostatic interactions and can be

Prof. Katsuhiko Ariga received his Ph.D. from the Tokyo Institute of Technology in 1990. He is currently the Leader of the Supermolecules Group and Principal Investigator at the World Premier International Research Centre for Materials Nanoarchitectonics, NIMS. He has also been appointed Professor at the University of Tokyo.



Dr. Eungjin Ahn has been undertaking post-doctoral research in the group of Dr. Byeong-Su Kim at Yonsei University since September 2018. He received his Ph.D. from the Department of Energy Engineering, Ulsan National Institute of Science and Technology (UNIST). His research interests are focused on carbon nanomaterials for applications in functional membranes and energy conversion.

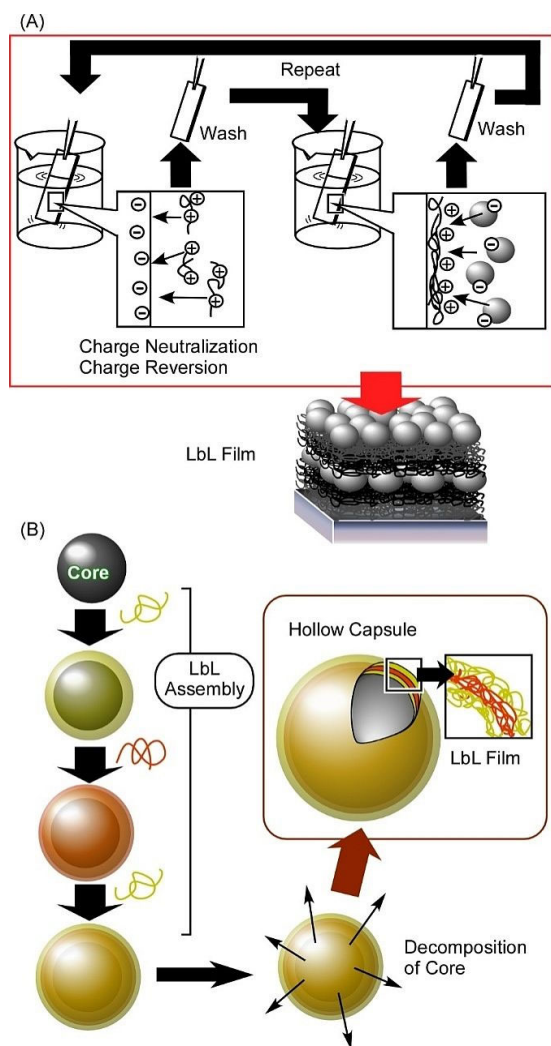


Minju Park is currently a Ph.D. student in the Department of Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST). She obtained her Bachelor's degree from the School of Energy and Chemical Engineering, UNIST. Her scientific interests are focused on the synthesis of carbon-based nanomaterials for organic reactions and energy devices.



Dr. Byeong-Su Kim is an Associate Professor in the Department of Chemistry at Yonsei University. He received his B.S. in Chemistry from Seoul National University in 1999 and his Ph.D. in Chemistry from the University of Minnesota in 2007. After completing postdoctoral research at MIT, he started his independent career at UNIST in 2009 and moved to Yonsei University in 2018. The Kim group is interested in the application of macromolecular chemistry to the study of new polymeric and hybrid nanomaterials, including the molecular design and synthesis of self-assembled polymers, layer-by-layer assembly for functional thin films, and complex macromolecular systems, such as carbon nanomaterials.





Scheme 2. Fundamental principles of LbL assembly: A) LbL assembly with electrostatic interactions on a solid surface; B) LbL assembly on a colloidal core and the preparation of hollow capsules.

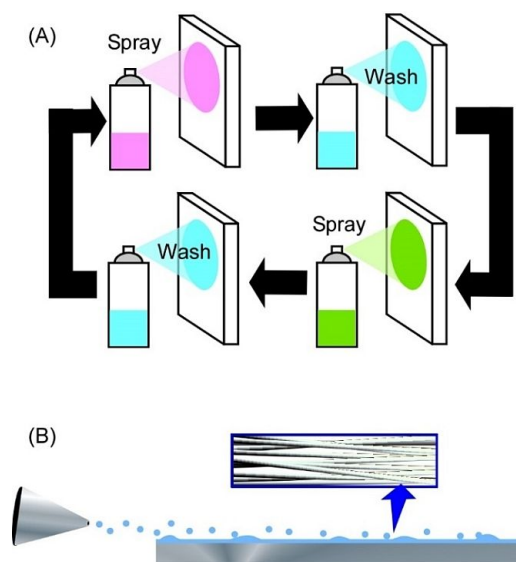
extended to other interactions, such as hydrogen-bonding interactions,^[35] biospecific interactions,^[36] metal coordination,^[37] charge transfer,^[38] supramolecular inclusion,^[39] stereocomplex formation,^[40] and sol/gel reactions.^[41] In addition, the technical aspects of this method are not limited to hand-processed dipping. Automated machines for LbL assembly^[42] and combined processes with spin-coating^[43] have also been proposed.

Architectures that can be fabricated by using LbL assembly are not limited to thin films on a flat substrate on the visible scale. Because of the broad versatility of LbL assembly, layering an assembly on invisibly small objects, such as colloidal particles, is also possible (Scheme 2B). Similarly to LbL assembly on a visible flat substrate, layered thin films can be sequentially assembled onto colloidal particles,^[44] and destruction of the colloidal cores after LbL assembly can result in the formation of hollow microcapsules. Because LbL microcapsules are capable of the inclusion of drug molecules and biomaterials in their inner cavities, as well as modification of their shells and surfaces, they offer significant potential for biomedical usages, such as drug delivery.^[45]

3. Innovations in LbL Assembly

3.1. Methodological Innovation: Physical Methods

Because the operational mechanisms of LbL assembly are simple and can be adapted to a variety of situations, the modification of LbL processes has been widely investigated. One of the most influential advancements in LbL techniques is known as the “spraying LbL” method (Scheme 3A). As presented by



Scheme 3. Grazing incidence spraying on a solid surface for the preparation of thin films of silver nanowires with in-plane anisotropy.

Schlenoff et al., instead of dipping a solid substrate into solutions of the target components, solutions of components such as polyelectrolytes were alternately sprayed onto a solid substrate, with intermediate rinsing by spraying with water.^[46] They demonstrated the fabrication of polyelectrolyte LbL multilayer films of poly(styrene sulfonate) and poly(diallyldimethylammonium chloride) and this spraying method offered the rapid fabrication of large-area LbL films, whilst maintaining high uniformity and good quality.

Decher and co-workers systematically compared LbL films that were prepared by using the conventional dipping procedure with those that were prepared by using the spraying method under various conditions, including component concentrations, spraying time, and drying time between depositions.^[47] They found that, even though the assembly processes with the spraying LbL method were very rapid, the thickness of the LbL films still increased linearly with the number of deposition cycles, similar to conventional dipping. Furthermore, the films that were prepared by using the spraying LbL technique were confirmed to possess low surface roughness upon evaluation by using AFM and X-ray reflectometry. In fact, the quality of the LbL films that were prepared by using the spraying method, with a preparation time of only 60 seconds per layer, was the same or better than that obtained by dipping an LbL film with a preparation time of 1520 seconds per layer,

thus indicating a 25-fold acceleration in film preparation by using the spraying LbL method. For LbL films of acceptable quality, the acceleration in film preparation increased to a factor of more than 250 versus dipping.

This spraying method also highlights the advantage of fabricating thin films with high in-plane anisotropy and orientation, as reported by Pauly and co-workers (Scheme 3B).^[48] The authors performed a spray-assisted deposition of silver nanowires by using a “grazing incidence spraying” technique on a solid surface. This simple modification presented immense advantages in controlling the in-plane density and orientation of the films. Typically, four-layer films of silver nanowires in the same in-plane direction showed a polarization efficiency of up to 97% in the near-infrared region. A combination of this grazing incidence spraying method with LbL assembly can create opportunities for nanoarchitectonics from multiple components with controlled in-plane orientation, because the film composition, component density, and orientation of each layer can be independently controlled. These characteristics are advantageous for nanoarchitected thin-film materials for a range of applications, including sensors, optoelectronic devices, conductive electrodes, and solar cells.

As observed in the spin-coating-assisted LbL method, the rotation of a solid substrate can also be performed with the LbL assembly process. An and co-workers conceptually converted this strategy into an LbL technique under high-gravity fields by employing a strong centrifugal force.^[49] The high-gravity field promoted the diffusion of the components, which increased the efficiency of adsorption, presumably owing to an increase in the concentration gradient and intensification of the turbulence. Although the LbL processes were hastened, the quality of the assembled films was maintained and was similar to that of films that were prepared by using conventional dipping.

Recently, Matsuba et al. reported a one-pot, spin-coating method for the fabrication of high-quality 2D films within 1 minute over a wide area.^[50] Under the influence of centrifugal force, nanosheet pieces were assembled in a 2D space without overlapping. Optimizing the spin-coating conditions, such as precursor concentration and rotation speed, led to high-quality films of a range of 2D materials, including metal-oxide nanosheets, GO, and reduced graphene oxide (rGO). Repeated cycles of optimized spin-coating and moderate-temperature heat treatment afforded multilayer LbL films of high quality. Because of the wide usage of spin-coating in industrial manufacturing, further consideration of the scaling-up of this method would allow the industrial-level production of LbL functional structures.

3.2. Methodological Innovation: Chemical Reactions and Interactions

The driving forces for LbL assembly are not limited to noncovalent interactions; rather, well-regulated chemical reactions can also be used to connect neighboring nanolayers to rationally nanoarchitect LbL functional structures. One example is the introduction of click chemistry into LbL processes, as reported by Caruso et al.^[51] This method involves the Cu^I-catalyzed

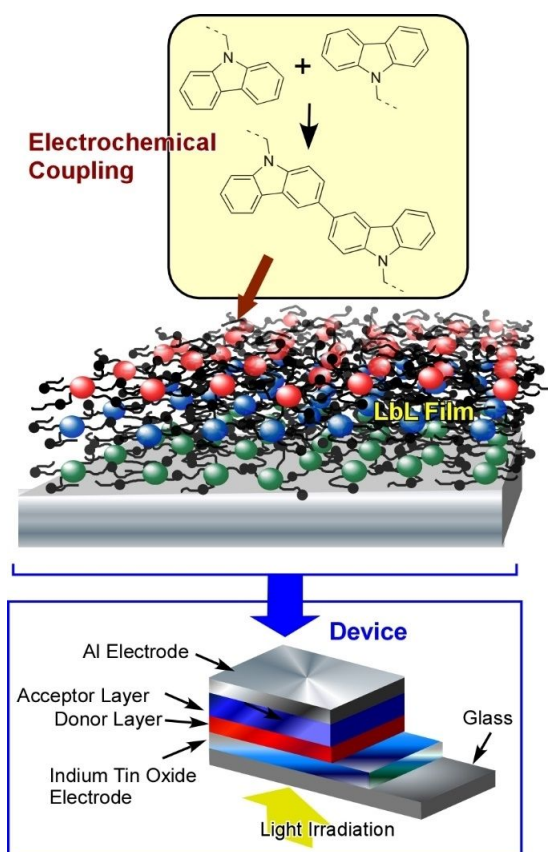
1,3-dipolar cycloaddition of azides to alkynes to form 1,2,3-triazoles, which typically has a high reaction yield and is performed under mild conditions in water. The triazole linkages are also sufficiently stable towards hydrolysis, oxidation, and reduction. Upon appropriate modification, click chemistry can also be applied to the formation of covalent connections with a variety of materials, including polymers, biomaterials, nanoparticles, and dye molecules. Therefore, the introduction of click chemistry into LbL processes would expand the possibilities of LbL architectures without losing its wide applicability. This “click LbL” method can also be applied to components without electrostatic and hydrogen-bonding capabilities and used for the construction of thin films from single components.

As an advanced method, Rydzek et al. reported a simultaneous electropolymerization and electro-click functionalization process for LbL assembly.^[52] In this method, an electrochemical stimulus that was generated by using cyclic voltammetry oxidized 4-azidoaniline and reduced Cu^{II} ions to trigger the polymerization of 4-azidoaniline and induce a click chemistry reaction, that is, a one-pot Cu^I-catalyzed alkyne–azide cycloaddition reaction. This procedure allowed continuous film growth for up to 450 cycles of cyclic voltammetry. This method is useful for LbL assembly with a desirable timing and offers several avenues for surface functionalization.

Another stimulus-controlled LbL process was reported by Li et al., who demonstrated an electrochemical-coupling layer-by-layer (ECCLbL) assembly, in which the dimerization of *N*-alkylcarbazole was triggered by an electrochemical stimulus from an electrode surface (Scheme 4).^[53] By modifying the monomer units of *N*-alkylcarbazole derivatives, a variety of functional units, such as porphyrins, fullerenes, and fluorenes, could be deposited as homo and heterolayers with the desired thicknesses and in the desired sequences by simply using electrochemical stimuli. Because additional reagents are not required and LbL electronic communication is well-ensured, thin-film-device nanoarchitectonics can be performed under clean and mild conditions. The regulated layering of donor and acceptor components has been successfully applied to p–n heterojunction devices and their photovoltaic functions.

Metal coordination has also been employed in LbL assembly for the regulated preparation of layered nanoarchitectures of metal–organic frameworks (MOFs). Shekhah et al. demonstrated a step-by-step formation of MOF layers on a solid surface.^[54] First, they modified a gold surface with mercaptohexadecanoic acid to afford exposed COOH groups. Then, copper(II)acetate and 1,3,5-benzenetricarboxylic acid were added in a stepwise manner to provide layer-by-layer MOF structures. This LbL formation of MOFs could be performed at room temperature and provided high crystallinity comparable to bulk MOFs.

Makiura et al. demonstrated the formation of a 2D MOF at an air/water interface as an analogous method to the LB technique.^[55] The as-prepared 2D MOF nanosheets were subsequently assembled into layer-by-layer structures. First, the formation of 2D MOF nanosheets was achieved by spreading a solution of [5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinato]cobalt(II) and pyridine in chloroform/methanol onto an aqueous



Scheme 4. ECCLBL assembly based on the dimerization of *N*-alkylcarbazole, triggered by an electrochemical stimulus from an electrode surface, and its application in a p-n heterojunction device for photovoltaic functions.

ous solution that included CuCl_2 . The nanosheets were assembled sequentially in an LbL manner with intermediate rinsing. This procedure could also be performed under ambient conditions and is advantageous for the fabrication of nanotechnological devices with MOF structures.

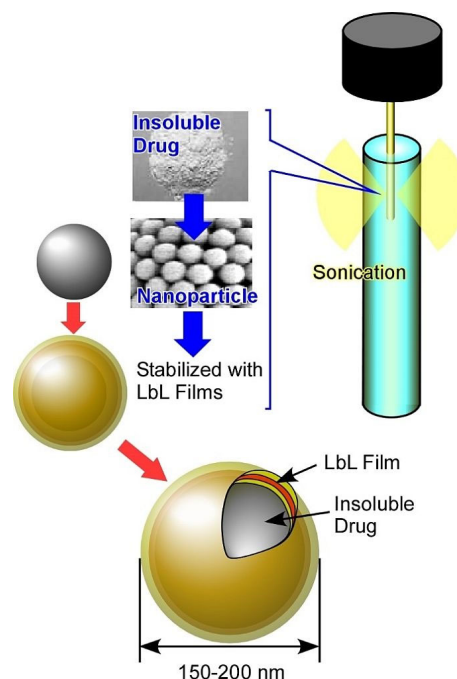
Recently, Yamauchi and co-workers reported the spontaneous one-pot formation of a LbL assembly from coordination polymers and GO.^[56] As a basic step, nickel-based cyanobridged coordination polymers were deposited onto the surface of GO nanosheets. In this case, GO acted a nucleation site for the growth of the coordination polymers, and the as-formed polymers bound to the GO nanosheets, thereby resulting in alternating LbL structures of heterogeneous nanosheets in a one-pot process. This approach could be applied to other inorganic materials to synthesize heterogeneous LbL nanoarchitectures with a range of functions.

3.3. Methodological Innovation: Biomedical and Biological Aspects

The use of LbL microcapsules in biomedical applications have received significant attention, with a focus on improving the applicability of LbL capsules for practical medical situations, as described briefly herein. Although LbL microcapsules are rather large in size (diameter: 3–5 μm), decreasing their size to

diameters of about 100 nm (as LbL nanocapsules) would allow their intravenous injection. Capsules that can contain a large number of anticancer drugs can be prepared by using such drugs with poor water solubility as nanocores, with the aid of ultrasound technologies. In addition, a modification of the LbL preparation methods to avoid the need for tedious rinsing has been proposed to simplify the LbL process for practical application. Furthermore, LbL nanocapsules have been nanoarchitected to exhibit higher resistance and longer blood-circulation time, mostly by employing the copolymerization of used polyelectrolytes with poly(ethylene glycol).

Lvov et al. developed a method for the formation of poorly water-soluble materials into nanocolloids that were covered with LbL films.^[57] Their method, termed “sonicated LbL encapsulation” (Scheme 5), involves the conversion of a dispersion of



Scheme 5. Ultrasound-induced LbL encapsulation: formulation of poorly water-soluble materials into nanocolloids (diameter: 150–200 nm) that are covered in LbL films.

poorly water-soluble materials into that of colloidal nanoparticles with diameters of 150–200 nm. The nanoparticles were stabilized by covering with polyelectrolytes. This strategy could be applied to a wide range of poorly water-soluble materials, such as anticancer drugs, anticorrosion agents, insoluble dyes, and inorganic salts. Additional coverage with polyelectrolyte LbL films dramatically improved the dispersion stability of the nanoparticles. This sonication-assisted LbL method would be beneficial for commercial targets, including pharmaceuticals, drug formulations, and in the paint industry.

Unlike LbL assemblies on a macroscopic flat surface, washing (rinsing) an LbL assembly to make the micro- and nano-scale colloidal particles invisible is not always easy. This process may involve tedious sample centrifugation and filtration. Therefore, a wash-less procedure is an important feature for

the industrial application of capsule-type LbL assembly. Lvov et al. demonstrated a wash-less process for the LbL assembly of nanocapsules by carefully monitoring the microparticle surface potential during the addition of the polyelectrolyte.^[58] They used the standard LbL assembly of poly(styrene sulfonate) and poly(allylamine) on the colloidal nanoparticles and, by performing *in situ* measurements of the surface charges of the colloidal particles, the appropriate moment for particle recharging was sensitively detected and then the polyelectrolyte species were immediately switched to avoid unnecessary over-adsorption. The successful preparation of LbL capsules without the need for a washing process was successfully achieved by carefully using this process, which could open up the industrial mass production of LbL capsules.

Versatility in the choice and design of membrane components in LbL assembly offers numerous possibilities for the surface modification of drug-carrier objects. Torchilin et al. imparted higher stability (longer resistance in blood) to nanostructured lipid carriers that were loaded with doxorubicin by using the LbL assembly of polyelectrolytes and coating with poly(ethylene glycol).^[59] The LbL-modified carriers showed lower accumulation in the liver, but higher accumulation in tumors, thereby leading to a significant inhibitory effect on tumor growth. As such, LbL structures can be optimized for particular target functions in fewer steps for the rapid production of more-efficient formulations.

LbL-based template synthesis is not limited to the use of spherical colloidal particles. For example, Li and co-workers demonstrated the fabrication of polyelectrolytes with a micro-tubular structure.^[60] The LbL method was used to assemble polyelectrolytes on the inner walls of pores of anodic aluminum oxide templates. Subsequent template removal resulted in the formation of microscopic tubes. Similarly, Komatsu et al. synthesized tubular structures by performing the LbL assembly of human serum albumin and poly-L-arginine by using a porous polycarbonate template.^[61] Hepatitis B virus particles were efficiently trapped by the swelled microtubes, followed by the significant removal of the corresponding genome DNA.

As elegant examples of nanoarchitectonics structures, Li and co-workers constructed biomimetic functional systems through the LbL assembly of biofunctional components. They demonstrated the first reconstitution of adenosine triphosphate synthase (ATPase) in assembled lipid-coated LbL polymer microcapsules (Figure 1).^[62] ATPase, as a biomolecular motor, can produce ATP, driven by a proton gradient. The nanoarchitected assembly could synthesize ATP from adenosine diphosphate (ADP) and phosphate. The same group also nanoarchitected ATPase-based energy-conversion systems that were immobilized on lipid-coated hemoglobin protein microcapsules through LbL assembly.^[63] In that case, the coexisting glucose oxidase (GOD) produced a proton gradient through the reaction of glucose with gluconolactone (gluconate). The fabricated biocompatible microcapsules could also be used for ATP storage.

Li et al. constructed light-harvesting nanoarchitectonics systems for better photophosphorylation performance by assembling biocomponents into a template-directed LbL assembly.^[64]

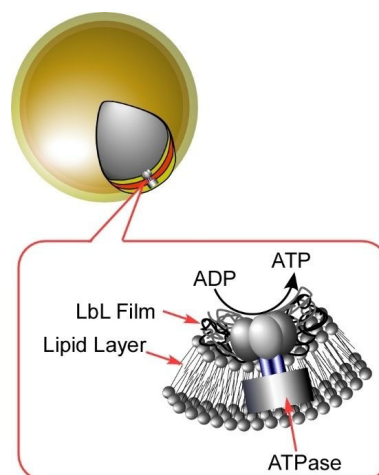


Figure 1. Reconstitution of adenosine triphosphate synthase (ATPase) in assembled lipid-coated LbL polymer microcapsules.

Polyelectrolyte LbL multilayers were assembled within the inner pores of a porous polycarbonate membrane, into which a silica-based hydrogel that contained photosystem II (PSII) was injected. After the template was removed, the proteoliposomes were coated with ATPase. The as-prepared light-harvesting nanoarchitectures had two photophosphorylation building blocks, PSII and ATPase. Water splitting by PSII upon light irradiation generated a proton gradient across the lipid membranes, which activated ATPase to produce ATP. These artificial systems exhibited significantly higher ATP-production rates than those that were observed in the chloroplasts.

3.4. Hierarchical Nanoarchitectures

As demonstrated by several examples, the LbL method holds great potential for the fabrication of hierarchical structures. Unlike the standard spontaneous self-assembly, the LbL method can combine spontaneous assembly and step-by-step directed assembly, which is advantageous for the production of hierarchical structures. First, organized nanostructures are fabricated by using an appropriate method, such as self-assembly and templated synthesis. Then, the as-formed organized nanostructures are further assembled into layered and then hierarchical structures by using the LbL technique.

Biological systems exhibit several features of hierarchical structures, and lipid bilayer membranes, cells, tissues, organs, and bionts are all constructed in a hierarchical manner. Katagiri et al. reported the synthesis of tissue mimics through the LbL assembly of artificial cell mimics.^[65] Liposomes and vesicles that are formed by the self-assembly of common lipids and amphiphiles are not always strong enough to maintain their spherical morphology during LbL assembly. To overcome this disadvantage, Katagiri et al. developed a new lipid bilayer vesicle with a surface siloxane framework, called a "cerasome" (ceramics+soma).^[66] Because of the silica-like framework on the surface, the cerasome has a negative surface charge and sufficient strength to tolerate strong electrostatic interactions with cationic polyelectrolytes. Therefore, LbL assembly between

anionic cerasome and poly(diallyldimethylammonium chloride) was successfully achieved without structural damage of their cell-like structures. Furthermore, the LbL assembly of anionic cerasome and cationic cerasome without the need for a polyelectrolyte was also demonstrated.^[67] These hierarchical structures could be regarded as tissue mimics upon the organized assembly of artificial cells.

The LbL assembly of pre-synthesized mesoporous materials can afford hierarchical structures. For this purpose, a mesoporous carbon material was first surface-oxidized to carry negative charges and then alternately assembled with a cationic polyelectrolyte to obtain a hierarchical LbL structure.^[68] A mass-sensitive quartz crystal microbalance (QCM) sensor that was coated with the as-prepared hierarchical LbL mesoporous carbon material exhibited selectivity towards tannic acid in the aqueous phase, presumably owing to size matching between the nanochannels and the size of the guest tannic acid molecules. The highly cooperative nature of the adsorption of tannic acid onto the nanopores in the hierarchical LbL structures was also confirmed.

The LbL assembly of mesoporous carbon capsules with polyelectrolytes into hierarchical structures and their application as a gas-phase sensor was reported by Ji et al. (Figure 2).^[69] A zeolite-templated synthesis provided mesoporous carbon capsules that exhibited a hierarchical structure, with capsular motifs and mesoporous channels in their shells. Surfactant-covered mesoporous carbon capsules were alternately assembled with a

counterionic polyelectrolyte into hierarchic LbL films on a QCM electrode. The sensor was covered with the carbon-capsule LbL films and subjected to organic vapor sensing. The sensor exhibited selectivity for aromatic vapors compared to aliphatic ones. In addition, doping the carbon capsules with a second sensory component dramatically altered the selectivity of the sensor. Similarly, hierarchical LbL films were also prepared from mesoporous silica capsules by using silica nanoparticles and polyelectrolytes.^[70] The as-prepared LbL films were applicable as material (drug)-delivery systems with stimuli-free automatic ON/OFF behavior.

LbL assembly is capable of fabricating atomically precise artificial layered structures that cannot be obtained from naturally occurring materials. Sasaki and co-workers prepared superlattice layers from layered-double-hydroxide nanosheets of $Mg_{2/3}Al_{1/3}(OH)_2$ and oxide nanosheets, such as $Ti_{0.91}O_2$ and $Ca_2Nb_3O_{10}$.^[71] These materials were separately exfoliated in solution and then alternately assembled into LbL restacked films. Such artificial superlattice structures could not be obtained by simply mixing the two components; instead, simple mixed just afforded lamellar flocculates with two lattice spacings of the original components. In contrast, the superlattice structures exhibited their own single-lattice spacing, which was the sum of two independent nanosheets. This simple-but-impressive example clearly demonstrates the potential for creativity in the production of new materials with an artificial superlattice.

Not limited to later lattice structures, LbL assembly can also dramatically modify the mixing states of two components, as demonstrated by Kotov and co-workers for hybrid materials of single-walled carbon nanotubes and polyelectrolytes.^[72] The inferior mechanical properties of hybrid materials of single-walled carbon nanotubes and polymers often originate from their poor connectivity and unfavorable phase separation. These disadvantages can be fixed by performing a sequential LbL assembly of these components, combined with chemical crosslinking. The obtained hybrid membranes could be delaminated from a solid substrate with an exceptionally strong, ceramic-like mechanical nature.

As an unusual example of LbL assembly, Yamauchi and co-workers reported the fabrication of all-metal LbL films, mesoporous bimetallic (Pt/Pd) multilayer films, by using a combined strategy of LbL assembly and electrochemical deposition (Figure 3A).^[73] The structures of the fabricated films had several advantages, including a large-area Pt/Pd heterointerface for advanced functions and mesoporous structures for facile material diffusion. In the LbL electrochemical deposition process, the solutions included surfactants to assist with micelle assembly, thereby resulting in the formation of mesoporous structures in the assembled films. The accessible nature of the Pt/Pd heterointerface, with high surface area of each layer, led to enhanced electrochemical activity in the methanol-oxidation reaction.

Ji et al. reported the fabrication of thin films that comprised LbL structures of rGO and an ionic liquid, and their application in gas sensing (Figure 3B).^[74] First, GO nanosheets were dispersed and reduced into rGO in the presence of an ionic liquid, such as an imidazolium salt. Because of the high affinity of graphene nanosheets for aromatic ionic liquids, alternate

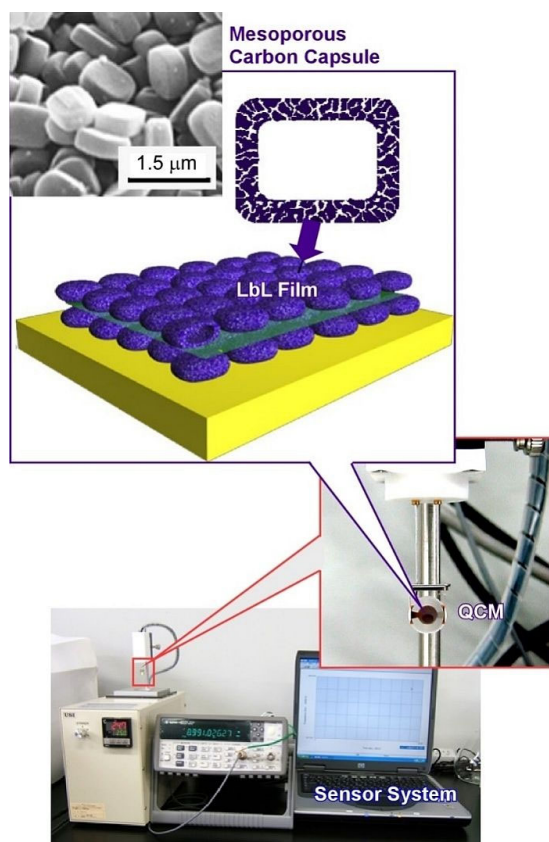


Figure 2. LbL assembly of mesoporous carbon capsules and a polyelectrolyte into hierarchical structures on a QCM electrode for sensing applications.

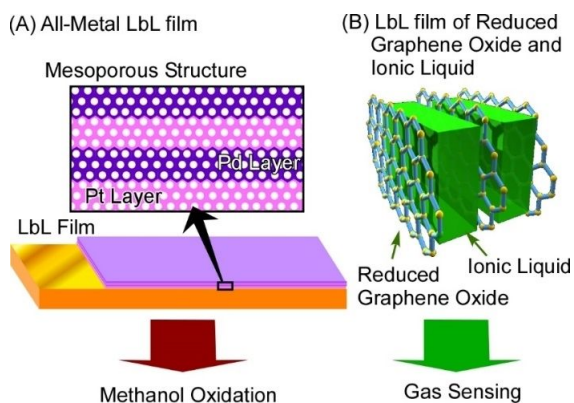


Figure 3. A) All-metal LbL film with mesoporous Pd and Pt layers; B) LbL film of rGO and an ionic liquid.

layers of rGO and the ionic liquid formed spontaneously. The as-formed layered composites of rGO and the ionic liquid had a positive charge and could be assembled alternately with polyelectrolytes. LbL films that contained composites of rGO and the ionic liquid were immobilized onto a QCM sensor electrode. The LbL QCM sensor exhibited notably high sensitivity to aromatic vapor, because the nanospaces between the rGO nanosheets that were filled with an aromatic ionic liquid were a π -electron-rich environment. Interestingly, the sensitivity for benzene vapor was more than 10-times higher than that for cyclohexane vapor, although these compounds had similar molecular sizes, molecular weights, and vapor pressures.

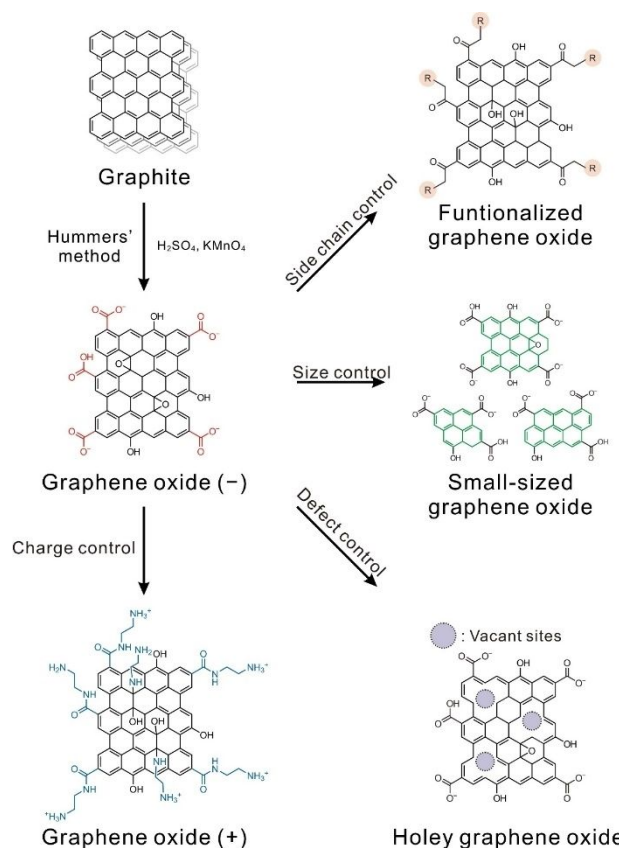
As an unusual combination of LbL assemblies, Leong and co-workers demonstrated an alternate assembly of 2D MoS₂ nanosheets and DNA for drug delivery.^[75] The MoS₂ nanosheets were modified with DNA oligonucleotides, which were then assembled by using linker aptamers into LbL structures. This LbL-assembled structure was capable of accommodating anticancer reagents, which were protected from external disturbances within the LbL assembly. Because the aptamer had a high affinity for ATP, the LbL structures disassembled to release the anticancer drugs in ATP-rich environments, such as cancer cells. This system enables the highly efficient apoptosis of cancer cells.

4. LbL Assembly: A Case Study of Graphene Oxide

In the previous sections, recent progress in LbL assembly was introduced systematically and briefly to demonstrate the versatility and potential of LbL assembly for a wide range of materials and applications. Unlike previous sections, the following sections will describe the availability and usefulness of LbL assembly for two specific materials, GO, and rGO, to systematically elucidate their features in greater detail. At present, the application of LbL assembly to energy-related fields is receiving a great deal of attention. The potential of new nano- and carbon-related materials has attracted significant interest, with the aim of achieving better performance for applications in energy devices and functional membranes.^[53,76] Many scientific

and technological advancements have been made by using LbL assembly for GOs and related materials.

GO is an oxidized intermediate material that is derived from pristine graphene, and is considered a transitional state for harnessing the superior properties of graphene nanosheets. GO consists of a single-layered carbon lattice that contains defects and other heteroatoms. It is typically produced by the chemical treatment of graphite through oxidation for exfoliation and stable dispersions in water or appropriate organic solvents. GO can be modified into various materials based on its unique chemical structure (Scheme 6). The oxygen functional groups in GO are predominantly hydroxy and epoxy groups in the basal plane, whilst carboxy, carbonyl, and quinone groups are present at its edge sites. These functional groups on GO can be utilized for further chemical reactions.



Scheme 6. Pathways for the fabrication of a variety of chemically modifiable GO derivatives.

Many studies have demonstrated the covalent functionalization of GO with other chemical moieties, such as sulfonyl acids, aromatic groups, and ionic liquids, by utilizing diazonium chemistry, π - π interactions, and silanization, respectively. For example, Kim and co-workers reported a simple approach in which amine functional groups were attached to carboxylic groups by using carbodiimide coupling to generate positively charged GO nanosheets. Such positively charged GO nanosheets are necessary for LbL assembly with negatively charged polymers and nanoparticles; as such, this approach has signifi-

cantly expanding the LbL toolkit.^[77–80] Various organic compounds/GO hybrid materials have been created by using physicochemical approaches, thereby improving the processability of these materials in different solvents and utilizing the outstanding properties of the attached molecules.^[81] A wide range of organic compounds, including aromatic dyes, ionic liquids, and pyrene derivatives, have also been anchored onto GO nanosheets, either in a covalent or noncovalent manner, for applications in catalysis, electronic devices, and solar cells. Such GO-based chemistry typically results in interesting properties and is promising for applications that require high chemical stability of the basal plane and tunable moieties at the multifunctional edge sites.

In the process of synthesizing GO from graphene, oxidative additives and reaction time significantly affect the sheet size and defect density on the basal plane. The sheet size of GO can be strategically chosen considering the end use, by modifying the basal plane or edge sites of the GO nanosheet. For instance, weakly oxidized GO contains relatively few functional groups within a large and relatively intact basal plane, which is suitable for membrane assemblies and applications that require good mechanical and electronic properties. Conversely, harshly oxidized GO contains several functional groups along with small sheet dimensions, which make it more appropriate for catalytic uses and applications that require functional groups to interact with other chemical moieties.

The drawbacks of using GO nanosheets in practical applications are its limited ion-transport pathways and slow ion-transport kinetics. To overcome these limitations, size-controlled or holey GO nanosheets can be used in nanomembrane assemblies, because they provide a controllable tortuosity and diffusion coefficient depending on the nanosheet structure. Size-controlled and holey GO have shown great potential for electrochemical applications, such as catalysis, batteries, and supercapacitors, in which high mass transport is required.

Unlike our previous reviews,^[82] herein, we will summarize recent progress in LbL-assembled GO-based thin-film electrodes and membranes for applications in the fields of materials science and electrochemistry, in particular from the viewpoint of our own research efforts over the past nine years.

4.1. Fine-Structural Nanoarchitectonics

Because of the unique properties of GO, GO nanosheets serve as an excellent platform for the fabrication of multilayer thin films that contain new metallic or inorganic nanomaterials as part of a nanoarchitectonics strategy.^[83–85] Layered nanostructures can immobilize functional nanoparticles within defined structures, which is useful for preparing materials for specific applications. Furthermore, GO nanosheets potentially improve the utilization and dispersion of nanoparticles through their high catalytic surface area and electronic conduction. Herein, we will highlight how the nanoarchitectonics of LbL assemblies can be precisely controlled to improve their properties and catalytic performance. Furthermore, nanoarchitectonics also opens a new avenue for the development of versatile LbL-assembly strategies for a range of applications (Figure 4).

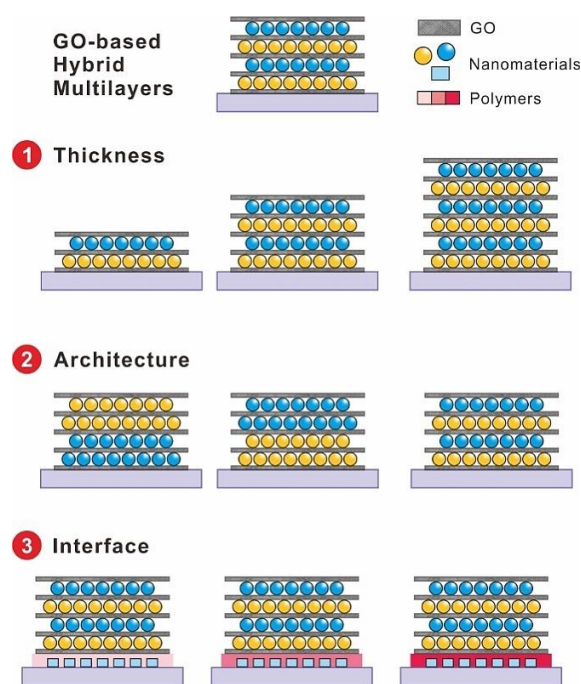


Figure 4. Schematic representation of controlling nanoarchitectonics within LbL-assembled GO/nanomaterial multilayers.

The performance of LbL-assembled multilayers is dependent on the number of layers, which is closely related to the film thickness.^[79,86,87] The LbL-assembly technique enhances the stability of nanoparticles on graphene sheets and can be used to control the performance of graphene-based hybrid multilayers by adjusting the number of layers. Several studies have demonstrated that controlling the thickness of LbL-assembled hybrid films significantly affects their activity, such as in methanol oxidation.^[83] We reported an integration of electroactive Au nanoparticles with GO nanosheets by using LbL assembly for the preparation of a 3D electrocatalytically active multilayer for methanol oxidation. The electrocatalytic activity gradually improved with increasing film thickness, owing to the higher concentration of active nanoparticles within the films. However, the electrocatalytic performance began to decrease after a critical number of bilayers (i.e., thickness), owing to decreasing mass transfer of the active materials. In agreement with observations reported elsewhere, the optimum thickness varied with a given set of reaction conditions, components, and structures of the LbL assembly.^[77,79,88] This observation highlights the importance of LbL assemblies, which offer precise control over electrode architecture to achieve optimal performance of the assembled nanoscale composite materials.

As a representative example, we reported the fabrication of LbL-assembled electrocatalytic thin films for methanol oxidation by adjusting the assembly sequence of LbL films that were composed of Au and Pd nanoparticles on GO nanosheets.^[84] Interestingly, even with an identical composition of nanoparticle constituents, the hybrid 3D films exhibited very different catalytic activities, depending on the electrode architecture. When the Au nanoparticles were located on the outer layer and the Pd nanoparticles were located on the inner layer,

the LbL electrodes showed much better electrocatalytic performance with a higher current density. This result demonstrated that LbL-assembled electrodes can provide an excellent model for nanoarchitectonics in terms of thin-film electrochemistry. The relative positions of the Au and Pd nanoparticles within the multilayer electrode afforded highly controllable electrocatalytic activity, thereby confirming the versatility of LbL assemblies for tuning the nanoscale architecture of hybrid electrodes.

So far, we have discussed tuning the active layers of LbL films to optimize catalytic performance. Unexpectedly, besides the active layers, we found that the base layer that is deposited prior to the catalytic multilayers also significantly influences catalytic activity. For example, a water-oxidation photoanode was fabricated through the tailored assembly of GO nanosheets and a cobalt polyoxometalate catalyst into a nacre-like multilayer architecture on hematite.^[80] When a base layer of a polyelectrolyte complex was deposited onto the surface, a large shift in the flat-band potential was observed, owing to the creation of a local dipole moment at the surface. As a result, the overall water-splitting reaction was enhanced by tuning the band edge to a more favorable position for efficient charge separation. This approach, which utilized surface tuning and catalytic multilayers, provides another example of the precise construction of nanoarchitectonics for highly efficient photoelectrodes and other devices for numerous applications. Whilst many of the preceding examples are graphene-based LbL assemblies, the nanoarchitectonics of LbL assemblies is not limited to the components and methods described herein. The key concept of nanoarchitectonics can be established by using a range of strategies and the design of new materials to improve performance for a variety of applications can be achieved.

4.2. Applications

To take advantage of the superior properties of these graphene-based LbL systems, including their conductivity, transmittance, and physicochemical stability, the nanoarchitectonics of associated material systems and devices is essential. Several modification steps are required to transform graphite into GO and, eventually, into rGO, which would allow for the preservation of some of these abovementioned advantages of graphene. Because individually dispersed GO nanosheets lack the required connections between the components for electron transfer, multilayer deposition by using LbL assembly has been employed to enhance the crosslinking and create a fully conductive thin film (Figure 5). One advantage of this approach is that the thickness of the multilayered thin film can be precisely controlled on the subnanometer scale by changing the number of deposition cycles. Ultrathin rGO multilayers that maintained a balance between the desired optical and electrical properties were possible by using an optimized deposition thickness on a glass substrate. The best performance of the rGO multilayer was observed with a low sheet resistance at a fine transmittance through electrostatic assembly between oppositely charged exfoliated rGO nanosheets.^[87]

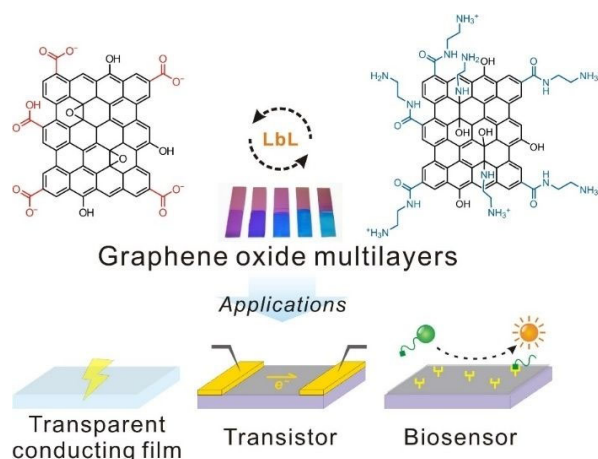


Figure 5. Applications of LbL-assembled GO multilayers.

During the thermal reduction of GO multilayers into rGO films, we discovered an atom-doping effect, in which nitrogen atoms from the amine functional groups of positively charged GO⁺ were incorporated into the rGO lattices, substituting for carbon atoms. Interestingly, this nitrogen-doping process occurred at various multilayer thicknesses, thereby inducing a transition in the electrical behavior of the resulting rGO multilayer transistors, that is, the charge-transport behavior changed from p-type to ambipolar and, eventually, to n-type with increasing film thickness. Unlike thermally reduced GO multilayers, chemically reduced GO films only showed ambipolar transport behavior. The charge-transport mechanism in the thermally prepared rGO multilayer was investigated, and the n-type dopant was found to fill the traps in the defect sites of the graphene lattice, which affected the electronic wave functions.^[77]

Based on its physicochemical stability, GO multilayered systems can also provide stable frameworks for a variety of chemical compounds. For example, a regularly arrayed GO multilayer was assembled on a glass substrate at a defined location in patterns that were suitable for the detection of target proteins.^[89] The efficient construction of fluorescent aptasensors requires the controlled proximity of dyes on GO multilayers, and the target compounds induce a corresponding fluorescence change in the sensor. Our GO-multilayer-based aptasensor was attached to a glass substrate by using electrostatic interactions, and the molecules that did not form covalent interactions on the GO spots were readily removed through simple rinsing. Interestingly, highly stacked GO multilayers were more sensitive towards the target protein, owing to high-density aptamer binding and effective fluorescence quenching on the GO surface. The benefits of a recyclable array of highly sensitive and readily processable GO sensors are immense. Thus, the microscopic control of GO components can be employed to operate an electronic device and to create a platform for efficient molecular sensing.

5. Future Perspectives

In this Minireview, we have summarized recent progress in the development of the LbL approach in two different ways: 1) by

collecting together short descriptions of a variety of different examples; and 2) by presenting a more-detailed summary of particular (GO-based) materials. The latter descriptions of LbL assemblies of GO nanosheets well-exemplifies the outstanding potential of the LbL technique for the construction of a range of functional structures from limited material species that can be well-adjusted to the target applications. The flexibility and adjustability of the LbL process can be extended to other materials and extensive further applications. For example, the LbL method has been employed in cell-surface engineering,^[90] which could have a significant impact on cell-based bioscience and biomedical technologies.^[91] Therefore, there needs to be greater exploration of new applications of this LbL technology as a near-future research goal. Another important key component in the development of this technique is the development of cheap mass-production processes for LbL materials.

This Minireview has emphasized the excellent versatility and applicability of the LbL method. A wide variety of materials can be assembled into a range of structures, including hierarchical structures. Furthermore, LbL assembly is capable of achieving rather irregular structures from multiple components, which cannot be fabricated by using other self-assembly methods. Furthermore, compared to these other methods, LbL assembly is also well-suited to the fabrication of more-complicated nanoarchitectures. The future direction of LbL assembly will involve its development from simple self-assembly into nanoarchitectonics. The preparation of highly functional materials that involve a sophisticated harmony of the component materials, as seen in biological systems, will require this nanoarchitectonics concept. We anticipate that LbL assembly will play an important role in the realization of the nanoarchitectonics concept in the future.

Acknowledgements

This study was supported by the JSPS KAKENHI (Grants-in-Aid for Scientific Research) "Coordination Asymmetry" (JP16H06518) and by the CREST program of the JST (JPMJCR1665). This work was also supported by the National Research Foundation of Korea (NRF-2017M3A7B4052802 and NRF-2018R1A5A1025208).

Conflict of interest

The authors declare no conflict of interest.

Keywords: graphene · layer-by-layer assembly · materials science · nanoarchitectonics · self-assembly

- [1] a) K. K. R. Datta, B. V. S. Reddy, K. Ariga, A. Vinu, *Angew. Chem. Int. Ed.* **2010**, *49*, 5961–5965; *Angew. Chem.* **2010**, *122*, 6097–6101; b) L. Zhang, E. Meggers, *Chem. Asian J.* **2017**, *12*, 2335–2342; c) K. Takimiya, M. Nakano, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 121–140; d) M.-H. Huang, W.-J. Hao, B. Jiang, *Chem. Asian J.* **2018**, *13*, 2958–2977; e) S. Cherumukkil, B. Vedhanarayanan, G. Das, V. K. Praveen, A. Ajayaghosh, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 100–120; f) Z. Sun, T. Matsuno, H. Isobe, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 907–921; g) Z. Sun, K. Ikemoto, T. M. Fukunaga, T.

- Koretsune, R. Arita, S. Sato, H. Isobe, *Science* **2019**, *363*, 151–155; h) J. Yamaguchi, K. Itami, *Bull. Chem. Soc. Jpn.* **2017**, *90*, 367–383; i) G. Povie, Y. Segawa, T. Nishihara, Y. Miyauchi, K. Itami, *Science* **2017**, *356*, 172–175.
- [2] a) K. Ariga, H. Ito, J. P. Hill, H. Tsukube, *Chem. Soc. Rev.* **2012**, *41*, 5800–5835; b) S. Stauss, I. Honma, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 492–505; c) A. Yamamura, S. Watanabe, M. Uno, M. Mitani, C. Mitsui, J. Tsurumi, N. Isahaya, Y. Kanaoka, T. Okamoto, J. Takeya, *Sci. Adv.* **2018**, *4*, eaao5758; d) E. Ruiz-Hitzky, A. Gómez-Avilés, M. Darder, P. Aranda, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 608–616; e) Y. Zhang, S. Yuan, G. Day, X. Wang, X. Yang, H.-C. Zhou, *Coord. Chem. Rev.* **2018**, *354*, 28–45; f) M. Nishizawa, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 1141–1149.
- [3] a) D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, *Science* **2016**, *351*, 361–365; b) Y.-P. Gao, K.-J. Huang, *Chem. Asian J.* **2017**, *12*, 1969–1984; c) T. Miyasaka, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 1058–1068; d) M. Watanabe, K. Dokko, K. Ueno, M. L. Thomas, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 1660–1682.
- [4] a) J. Shu, D. Tang, *Chem. Asian J.* **2017**, *12*, 2780–2789; b) J. Shi, P. W. Kantoff, R. Wooster, O. C. Farokhzad, *Nat. Rev. Cancer* **2017**, *17*, 20–37; c) K. Bhattacharyya, S. Mukherjee, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 447–454; d) G. van Niel, G. D'Angelo, G. Raposo, *Nat. Rev. Mol. Cell Biol.* **2018**, *19*, 213–228; e) T. Sawada, T. Serizawa, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 455–466; f) H. He, B. Xu, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 900–906.
- [5] a) W. Chaikittisilp, N. L. Torad, C. Li, M. Imura, N. Suzuki, S. Ishihara, K. Ariga, Y. Yamauchi, *Chem. Eur. J.* **2014**, *20*, 4217–4221; b) P. Zheng, N. Wu, *Chem. Asian J.* **2017**, *12*, 2343–2353; c) R. Sakamoto, *Bull. Chem. Soc. Jpn.* **2017**, *90*, 272–278.
- [6] a) J. Lu, M. Guo, J. Tang, *Chem. Asian J.* **2017**, *12*, 2772–2779; b) R. K. Ulaganathan, Y.-H. Chang, D.-Y. Wang, S.-S. Li, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 761–771; c) M. Suda, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 19–28; d) M. Irie, M. Morimoto, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 237–250.
- [7] a) Y. V. Kaneti, J. Tang, R. R. Salunkhe, X. Jiang, A. Yu, K. C.-W. Wu, Y. Yamauchi, *Adv. Mater.* **2017**, *29*, 1604898; b) Q. Wei, F. Xiong, S. Tan, L. Huang, E. H. Lan, B. Dunn, L. Mai, *Adv. Mater.* **2017**, *29*, 1602300; c) T. Shimizu, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 623–668; d) R. Chen, J. Kang, M. Kang, H. Lee, H. Lee, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 979–990.
- [8] a) M. C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293–346; b) J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103–1170; c) N. C. Seeman, H. F. Sleiman, *Nat. Rev. Mater.* **2018**, *3*, 17068.
- [9] a) K. Ariga, Q. Ji, W. Nakanishi, J. P. Hill, M. Aono, *Mater. Horiz.* **2015**, *2*, 406–413; b) K. Ariga, *ChemNanoMat* **2016**, *2*, 333–343; c) K. Ariga, T. Mori, L. K. Shrestha, *Chem. Rec.* **2018**, *18*, 676–695.
- [10] a) K. Ariga, Q. Ji, J. P. Hill, Y. Bando, M. Aono, *NPG Asia Mater.* **2012**, *4*, e17; b) K. Ariga, M. Aono, *Jpn. J. Appl. Phys.* **2016**, *55*, 1102A6.
- [11] a) K. Ariga, M. Li, G. J. Richards, J. P. Hill, *J. Nanosci. Nanotechnol.* **2011**, *11*, 1–13; b) K. Ariga, J. Li, J. Fei, Q. Ji, J. P. Hill, *Adv. Mater.* **2016**, *28*, 1251–1286; c) K. Ariga, K. Minami, M. Ebara, J. Nakanishi, *Polym. J.* **2016**, *48*, 371–389.
- [12] a) M. Aono, K. Ariga, *Adv. Mater.* **2016**, *28*, 989–992; b) K. Ariga, *Mater. Chem. Front.* **2017**, *1*, 208–211.
- [13] a) K. Ariga, D. T. Leong, T. Mori, *Adv. Funct. Mater.* **2018**, *28*, 1702905; b) K. Ariga, M. Nishikawa, T. Mori, J. Takeya, L. K. Shrestha, J. P. Hill, *Sci. Technol. Adv. Mater.* **2019**, *20*, 51–95; c) K. Ariga, X. Jia, L. K. Shrestha, *Mol. Syst. Des. Eng.* **2019**, *4*, 49–64.
- [14] a) K. Ariga, V. Malgras, Q. Ji, M. B. Zakaria, Y. Yamauchi, *Coord. Chem. Rev.* **2016**, *320–321*, 139–152; b) D. Sangian, Y. Ide, Y. Bando, A. E. Rowan, Y. Yamauchi, *Small* **2018**, *14*, 1800551; c) A. Azhar, Y. Li, Z. Cai, M. B. Zakaria, M. K. Masud, S. A. Hossain, J. Kim, W. Zhang, J. Na, Y. Yamauchi, M. Hu, *Bull. Chem. Soc. Jpn.* **2019**, *92*, 875–904.
- [15] a) M. Ramanathan, L. K. Shrestha, T. Mori, Q. Ji, J. P. Hill, K. Ariga, *Phys. Chem. Chem. Phys.* **2013**, *15*, 10580–10611; b) L. K. Shrestha, Q. Ji, T. Mori, K. Miyazawa, Y. Yamauchi, J. P. Hill, K. Ariga, *Chem. Asian J.* **2013**, *8*, 1662–1679; c) K. Ariga, T. Mori, W. Nakanishi, J. P. Hill, *Phys. Chem. Chem. Phys.* **2017**, *19*, 23658–23676; Y. Sang, M. Liu, *Mol. Syst. Des. Eng.* **2019**, *4*, 11–28.
- [16] a) S. Ishihara, J. Labuta, W. Van Rossom, D. Ishikawa, K. Minami, J. P. Hill, K. Ariga, *Phys. Chem. Chem. Phys.* **2014**, *16*, 9713–9746; b) M. Pandeewar, S. P. Senanayak, T. Govindaraju, *ACS Appl. Mater. Interfaces* **2016**, *8*, 30362–30371; c) M. Komiyama, T. Mori, K. Ariga, *Bull. Chem. Soc. Jpn.*

- 2018, 91, 1075–1111; J. A. Jackman, N.-J. Cho, M. Nishikawa, G. Yoshikawa, T. Mori, L. K. Shrestha, K. Ariga, *Chem. Asian J.* **2018**, 13, 3366–3377.
- [17] a) K. Ariga, S. Ishihara, H. Abe, M. Li, J. P. Hill, *J. Mater. Chem.* **2012**, 22, 2369–2377; b) C. M. Puscasu, G. Carja, C. Zaharia, *Int. J. Mater. Prod. Technol.* **2015**, 51, 228–240.
- [18] a) H. Abe, J. Liu, K. Ariga, *Mater. Today* **2016**, 19, 12–18; b) K. Ariga, S. Ishihara, H. Abe, *CrystEngComm* **2016**, 18, 6770–6778.
- [19] a) A. H. Khan, S. Ghosh, B. Pradhan, A. Dalui, L. K. Shrestha, S. Acharya, K. Ariga, *Bull. Chem. Soc. Jpn.* **2017**, 90, 627–648; J. Kim, J. H. Kim, K. Ariga, *Joule* **2017**, 1, 739–768; b) J. Xu, J. Zhang, W. Zhang, C.-S. Lee, *Adv. Energy Mater.* **2017**, 7, 1700571.
- [20] a) K. Ariga, S. Watanabe, T. Mori, J. Takeya, *NPG Asia Mater.* **2018**, 10, 90–106; b) J. M. Giussi, M. L. Cortez, W. A. Marmisollé, O. Azzaroni, *Chem. Soc. Rev.* **2019**, 48, 814–849.
- [21] a) K. Ariga, Q. Ji, T. Mori, M. Naito, Y. Yamauchi, H. Abe, J. P. Hill, *Chem. Soc. Rev.* **2013**, 42, 6322–6345; b) K. Ariga, K. Kawakami, M. Ebara, Y. Kotsuchibashi, Q. Ji, J. P. Hill, *New J. Chem.* **2014**, 38, 5149–5516; c) W. Nakanishi, K. Minami, L. K. Shrestha, Q. Ji, J. P. Hill, K. Ariga, *Nano Today* **2014**, 9, 378–394; d) M. Komiyama, K. Yoshimoto, M. Sisido, K. Ariga, *Bull. Chem. Soc. Jpn.* **2017**, 90, 967–1004; e) L. Zhao, Q. Zou, X. Yan, *Bull. Chem. Soc. Jpn.* **2019**, 92, 70–79.
- [22] a) K. Ariga, Y. Yamauchi, T. Mori, J. P. Hill, *Adv. Mater.* **2013**, 25, 6477–6512; b) X. Liu, J. G. Riess, M. P. Krafft, *Bull. Chem. Soc. Jpn.* **2018**, 91, 846–857; c) T. Seki, *Bull. Chem. Soc. Jpn.* **2018**, 91, 1026–1057; d) K. Ariga, T. Mori, J. Li, *Langmuir* **2019**, 35, 3585–3599.
- [23] a) K. Ariga, Y. Yamauchi, G. Ryzdek, Q. Ji, Y. Yonamine, K. C.-W. Wu, J. P. Hill, *Chem. Lett.* **2014**, 43, 36–68; b) G. Ryzdek, Q. Ji, M. Li, P. Schaaf, J. P. Hill, F. Boulmedais, K. Ariga, *Nano Today* **2015**, 10, 138–167.
- [24] G. Decher, *Science* **1997**, 277, 1232–1237.
- [25] R. K. Iler, *J. Colloid Interface Sci.* **1966**, 21, 569–594.
- [26] a) G. Decher, J.-D. Hong, *Makromol. Chem. Macromol. Symp.* **1991**, 46, 321–327; b) G. Decher, J. D. Hong, *Ber. Bunsen-Ges.* **1991**, 95, 1430–1434.
- [27] a) H. Lee, L. J. Kepley, H.-G. Hong, T. E. Mallouk, *J. Am. Chem. Soc.* **1988**, 110, 618–620; b) S. W. Keller, H.-N. Kim, T. E. Mallouk, *J. Am. Chem. Soc.* **1994**, 116, 8817–8818.
- [28] a) Y. Lvov, M. Onda, K. Ariga, T. Kunitake, *J. Biomater. Sci. Polym. Ed.* **1998**, 9, 345–355; b) D. Yoo, S. S. Shiratori, M. F. Rubner, *Macromolecules* **1998**, 31, 4309–4318; c) S. S. Shiratori, M. F. Rubner, *Macromolecules* **2000**, 33, 4213–4219; d) Y. Lvov, K. Ariga, M. Onda, I. Ichinose, T. Kunitake, *Colloids Surf. A* **1999**, 146, 337–346.
- [29] a) N. A. Kotov, I. Dékány, J. H. Fendler, *J. Phys. Chem.* **1995**, 99, 13065–13069; b) Y. Lvov, K. Ariga, I. Ichinose, T. Kunitake, *Langmuir* **1996**, 12, 3038–3044; c) Y. Lvov, K. Ariga, M. Onda, I. Ichinose, T. Kunitake, *Langmuir* **1997**, 13, 6195–6203.
- [30] a) Y. Lvov, K. Ariga, T. Kunitake, *Chem. Lett.* **1994**, 23, 2323–2326; b) Y. Lvov, K. Ariga, I. Ichinose, T. Kunitake, *J. Am. Chem. Soc.* **1995**, 117, 6117–6123; c) M. Onda, Y. Lvov, K. Ariga, T. Kunitake, *J. Ferment. Bioeng.* **1996**, 82, 502–506; d) M. Onda, Y. Lvov, K. Ariga, T. Kunitake, *Biotechnol. Bioeng.* **1996**, 51, 163–167.
- [31] Y. Lvov, H. Haas, G. Decher, H. Moehwald, A. Mikhailov, B. Mtchedlishvili, E. Morgunova, B. Vainshtein, *Langmuir* **1994**, 10, 4232–4236.
- [32] a) V. C. Rodrigues, M. L. Moraes, J. C. Soares, A. C. Soares, R. Sanfelice, E. Deffune, O. N. Oliveira Jr., *Bull. Chem. Soc. Jpn.* **2018**, 91, 891–896; b) Q. Ji, X. Qiao, X. Liu, H. Jia, J.-S. Yu, K. Ariga, *Bull. Chem. Soc. Jpn.* **2018**, 91, 391–397.
- [33] a) Y. Lvov, F. Essler, G. Decher, *J. Phys. Chem.* **1993**, 97, 13773–13777; b) K. Ariga, Y. Lvov, T. Kunitake, *J. Am. Chem. Soc.* **1997**, 119, 2224–2231.
- [34] a) K. Ariga, J. P. Hill, Q. Ji, *Phys. Chem. Chem. Phys.* **2007**, 9, 2319–2340; b) K. Ariga, Q. Ji, J. P. Hill, *Adv. Polym. Sci.* **2010**, 229, 51–87.
- [35] a) W. B. Stockton, M. F. Rubner, *Macromolecules* **1997**, 30, 2717–2725; b) L. Wang, Z. Wang, X. Zhang, J. Shen, L. Chi, H. Fuchs, *Macromol. Rapid Commun.* **1997**, 18, 509–514.
- [36] Y. Lvov, K. Ariga, I. Ichinose, T. Kunitake, *J. Chem. Soc. Chem. Commun.* **1995**, 2313–2314.
- [37] H. Xiong, M. Cheng, Z. Zhou, X. Zhang, J. Shen, *Adv. Mater.* **1998**, 10, 529–532.
- [38] Y. Shimazaki, M. Mitsuishi, S. Ito, M. Yamamoto, *Langmuir* **1997**, 13, 1385–1387.
- [39] A. Ikeda, T. Hatano, S. Shinkai, T. Akiyama, S. Yamada, *J. Am. Chem. Soc.* **2001**, 123, 4855–4856.
- [40] a) T. Serizawa, K.-i. Hamada, T. Kitayama, N. Fujimoto, K. Hatada, M. Akashi, *J. Am. Chem. Soc.* **2000**, 122, 1891–1899; b) T. Serizawa, K.-i. Hamada, M. Akashi, *Nature* **2004**, 429, 52–55.
- [41] I. Ichinose, T. Kawakami, T. Kunitake, *Adv. Mater.* **1998**, 10, 535–539.
- [42] a) S. L. Clark, P. T. Hammond, *Adv. Mater.* **1998**, 10, 1515–1519; b) S. S. Shiratori, M. Yamada, *Polym. Adv. Technol.* **2000**, 11, 810–814.
- [43] a) J. Cho, K. Char, J.-D. Hong, K.-B. Lee, *Adv. Mater.* **2001**, 13, 1076–1078; b) S.-S. Lee, K.-B. Lee, J.-D. Hong, *Langmuir* **2003**, 19, 7592–7596; c) S.-S. Lee, J.-D. Hong, C. H. Kim, K. Kim, J. P. Koo, K.-B. Lee, *Macromolecules* **2001**, 34, 5358–5360.
- [44] a) G. B. Sukhorukov, E. Donath, S. Davis, H. Lichtenfeld, F. Caruso, V. I. Popov, H. Möhwald, *Polym. Adv. Technol.* **1998**, 9, 759–767; b) E. Donath, G. B. Sukhorukov, F. Caruso, S. A. Davis, H. Möhwald, *Angew. Chem. Int. Ed.* **1998**, 37, 2201–2205; *Angew. Chem.* **1998**, 110, 2323–2327; c) F. Caruso, R. A. Caruso, H. Möhwald, *Science* **1998**, 282, 1111–1114.
- [45] K. Ariga, Y. M. Lvov, K. Kawakami, Q. Ji, J. P. Hill, *Adv. Drug Delivery Rev.* **2011**, 63, 762–771.
- [46] J. B. Schlenoff, S. T. Dubas, T. Farhat, *Langmuir* **2000**, 16, 9968–9969.
- [47] A. Izquierdo, S. S. Ono, J.-C. Voegel, P. Schaaf, G. Decher, *Langmuir* **2005**, 21, 7558–7567.
- [48] H. Hu, M. Pauly, O. Felix, G. Decher, *Nanoscale*, **2017**, 9, 1307–1314.
- [49] L. Ma, M. Cheng, G. Jia, Y. Wang, Q. An, X. Zeng, Z. Shen, Y. Zhang, F. Shi, *Langmuir* **2012**, 28, 9849–9856.
- [50] K. Matsuba, C. Wang, K. Saruwatari, Y. Uesusuki, K. Akatsuka, M. Osada, Y. Ebina, R. Ma, T. Sasaki, *Sci. Adv.* **2017**, 3, e1700414.
- [51] G. K. Such, J. F. Quinn, A. Quinn, E. Tjipto, F. Caruso, *J. Am. Chem. Soc.* **2006**, 128, 9318–9319.
- [52] G. Ryzdek, T. G. Terentyeva, A. Pakdel, D. Golberg, J. P. Hill, K. Ariga, *ACS Nano* **2014**, 8, 5240–5248.
- [53] a) M. Li, S. Ishihara, M. Akada, M. Liao, L. Sang, J. P. Hill, V. Krishnan, Y. Ma, K. Ariga, *J. Am. Chem. Soc.* **2011**, 133, 7348–7351; b) M. Li, S. Ishihara, Q. Ji, Y. Ma, J. P. Hill, K. Ariga, *Chem. Lett.* **2012**, 41, 383–385.
- [54] O. Shekha, H. Wang, S. Kowarik, F. Schreiber, M. Paulus, M. Tolan, C. Sternemann, F. Evers, D. Zacher, R. A. Fischer, C. Wöll, *J. Am. Chem. Soc.* **2007**, 129, 15118–15119.
- [55] R. Makiura, S. Motoyama, Y. Umehura, H. Yamanaka, O. Sakata, H. Kitagawa, *Nat. Mater.* **2010**, 9, 565–571.
- [56] M. B. Zakaria, C. Li, Q. Ji, B. Jiang, S. Tominaka, Y. Ide, J. P. Hill, K. Ariga, Y. Yamauchi, *Angew. Chem. Int. Ed.* **2016**, 55, 8426–8430; *Angew. Chem.* **2016**, 128, 8566–8570.
- [57] Y. M. Lvov, P. Pattekari, X. Zhang, V. Torchilin, *Langmuir* **2011**, 27, 1212–1217.
- [58] G. Bantchev, Z. Lu, Y. Lvov, *J. Nanosci. Nanotechnol.* **2009**, 9, 396–403.
- [59] a) S. V. Mussi, G. Parekh, P. Pattekari, T. Levchenko, Y. Lvov, L. A. M. Ferreira, V. P. Torchilin, *Int. J. Pharm.* **2015**, 495, 186–193; b) T. G. Shutava, P. P. Pattekari, K. A. Arapov, V. P. Torchilin, Y. M. Lvov, *Soft Matter* **2012**, 8, 9418–9427.
- [60] S. Ai, G. Lu, Q. He, J. Li, *J. Am. Chem. Soc.* **2003**, 125, 11140–11141.
- [61] T. Komatsu, X. Qu, H. Ihara, M. Fujihara, H. Azuma, H. Ikeda, *J. Am. Chem. Soc.* **2011**, 133, 3246–3248.
- [62] L. Duan, Q. He, K. Wang, X. Yan, Y. Cui, H. Möhwald, J. Li, *Angew. Chem. Int. Ed.* **2007**, 46, 6996–7000; *Angew. Chem.* **2007**, 119, 7126–7130.
- [63] W. Qi, L. Duan, K. Wang, X. Yan, Y. Cui, Q. He, J. Li, *Adv. Mater.* **2008**, 20, 601–605.
- [64] G. Li, J. Fei, Y. Xu, Y. Li, J. Li, *Adv. Funct. Mater.* **2018**, 28, 1706557.
- [65] K. Katagiri, R. Hamasaki, K. Ariga, J. Kikuchi, *Langmuir* **2002**, 18, 6709–6711.
- [66] a) K. Katagiri, K. Ariga, J. Kikuchi, *Chem. Lett.* **1999**, 28, 661–662; b) K. Katagiri, M. Hashizume, K. Ariga, T. Terashima, J. Kikuchi, *Chem. Eur. J.* **2007**, 13, 5272–5281.
- [67] K. Katagiri, R. Hamasaki, K. Ariga, J. Kikuchi, *J. Am. Chem. Soc.* **2002**, 124, 7892–7893.
- [68] K. Ariga, A. Vinu, Q. Ji, O. Ohmori, J. P. Hill, S. Acharya, J. Koike, S. Shiratori, *Angew. Chem. Int. Ed.* **2008**, 47, 7254–7257; *Angew. Chem.* **2008**, 120, 7364–7367.
- [69] Q. Ji, S. B. Yoon, J. P. Hill, A. Vinu, J.-S. Yu, K. Ariga, *J. Am. Chem. Soc.* **2009**, 131, 4220–4221.
- [70] a) Q. Ji, M. Miyahara, J. P. Hill, S. Acharya, A. Vinu, S. B. Yoon, J.-S. Yu, K. Sakamoto, K. Ariga, *J. Am. Chem. Soc.* **2008**, 130, 2376–2377; b) Q. Ji, S.

- Acharya, J. P. Hill, A. Vinu, S. B. Yoon, J.-S. Yu, K. Sakamoto, K. Ariga, *Adv. Funct. Mater.* **2009**, *19*, 1792–1799.
- [71] L. Li, R. Ma, Y. Ebina, K. Fukuda, K. Takada, T. Sasaki, *J. Am. Chem. Soc.* **2007**, *129*, 8000–8007.
- [72] A. A. Mamedov, N. A. Kotov, M. Prato, D. M. Guldi, J. P. Wicksted, A. Hirsch, *Nat. Mater.* **2002**, *1*, 190–194.
- [73] H. Wang, S. Ishihara, K. Ariga, Y. Yamauchi, *J. Am. Chem. Soc.* **2012**, *134*, 10819–10821.
- [74] Q. Ji, I. Honma, S.-M. Paek, M. Akada, J. P. Hill, A. Vinu, K. Ariga, *Angew. Chem. Int. Ed.* **2010**, *49*, 9737–9739; *Angew. Chem.* **2010**, *122*, 9931–9933.
- [75] B. L. Li, M. I. Setyawati, L. Chen, J. Xie, K. Ariga, C.-T. Lim, S. Garaj, D. T. Leong, *ACS Appl. Mater. Interfaces* **2017**, *9*, 15286–15296.
- [76] S. A. Castleberry, W. Li, D. Deng, S. Mayner, P. T. Hammond, *ACS Nano* **2014**, *8*, 6580–6589.
- [77] H. Hwang, P. Joo, M. S. Kang, G. Ahn, J. T. Han, B.-S. Kim, J. H. Cho, *ACS Nano* **2012**, *6*, 2432–2440.
- [78] S. H. Yang, T. Lee, E. Seo, E. H. Ko, I. S. Choi, B.-S. Kim, *Macromol. Biosci.* **2012**, *12*, 61–66.
- [79] E. Ahn, B.-S. Kim, *ACS Appl. Mater. Interfaces* **2017**, *9*, 8688–8695.
- [80] Y. Choi, D. Jeon, Y. Choi, D. Kim, N. Kim, M. Gu, S. Bae, T. Lee, H.-W. Lee, B.-S. Kim, et al., *ACS Nano* **2019**, *13*, 467–475.
- [81] D. Li, W. Zheng, D. Zheng, J. Gong, L. Wang, C. Jin, P. Li, H. Bai, *ACS Appl. Mater. Interfaces* **2016**, *8*, 3977–3984.
- [82] a) J. Hong, J. Y. Han, H. Yoon, P. Joo, T. Lee, E. Seo, K. Char, B.-S. Kim, *Nanoscale* **2011**, *3*, 4515–4531; b) T. Lee, S. H. Min, M. Gu, Y. K. Jung, W. Lee, J. U. Lee, D. G. Seong, B.-S. Kim, *Chem. Mater.* **2015**, *27*, 3785–3796; c) E. Ahn, T. Lee, M. Gu, M. Park, S. H. Min, B.-S. Kim, *Chem. Mater.* **2017**, *29*, 69–79; d) D. Kim, M. Gu, M. Park, T. Kim, B.-S. Kim, *Mol. Syst. Des. Eng.* **2019**, *4*, 65–77.
- [83] Y. Choi, M. Gu, J. Park, H.-K. Song, B.-S. Kim, *Adv. Energy Mater.* **2012**, *2*, 1510–1518.
- [84] M. Gu, B.-S. Kim, *Nano Energy* **2016**, *30*, 658–666.
- [85] D. Jeon, H. Kim, C. Lee, Y. Han, M. Gu, B.-S. Kim, J. Ryu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 40151–40161.
- [86] P. Joo, K. Jo, G. Ahn, D. Voiry, H. Y. Jeong, S. Ryu, M. Chhowalla, B. Kim, *Nano Lett.* **2014**, *14*, 6456–6462.
- [87] D. W. Lee, T.-K. Hong, D. Kang, J. Lee, M. Heo, J. Y. Kim, B.-S. Kim, H. S. Shin, *J. Mater. Chem.* **2011**, *21*, 3438–3442.
- [88] J.-T. Chen, Y.-J. Fu, Q.-F. An, S.-C. Lo, S.-H. Huang, W.-S. Hung, C.-C. Hu, K.-R. Lee, J.-Y. Lai, *Nanoscale* **2013**, *5*, 9081–9088.
- [89] Y. K. Jung, T. Lee, E. Shin, B.-S. Kim, *Sci. Rep.* **2013**, *3*, 3367.
- [90] a) B. Franz, S. S. Balkundi, C. Dahl, Y. M. Lvov, A. Prange, *Macromol. Biosci.* **2007**, *7*, 877–882; b) R. F. Fakhrullin, V. N. Paunov, *Chem. Commun.* **2009**, 2511–2513; c) H. Lee, D. Hong, H. Cho, J. Y. Kim, J. H. Park, S. H. Lee, H. M. Kim, R. F. Fakhrullin, I. S. Choi, *Sci. Rep.* **2016**, *6*, 38517.
- [91] a) Y. Katayama, *Bull. Chem. Soc. Jpn.* **2017**, *90*, 12–21; b) W.-H. Lin, C.-Y. Lin, C.-C. Tsai, J. Yu, W.-B. Tsai, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 1457–1464; c) K. Ariga, X. Jia, J. Song, C.-T. Hsieh, S.-h. Hsu, *ChemNanoMat* **2019**, *5*, 692–702; d) J. Kobayashi, T. Okano, *Bull. Chem. Soc. Jpn.* **2019**, *92*, 817–824.

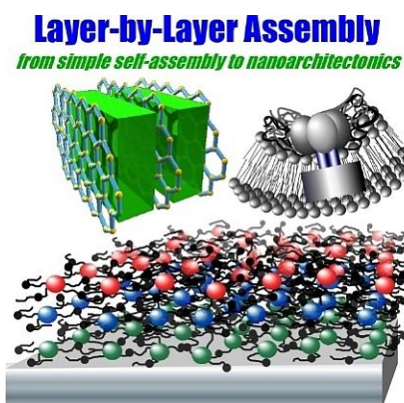
Manuscript received: May 10, 2019

Accepted manuscript online: June 6, 2019

Version of record online: ■■■■■, 0000

MINIREVIEW

Laying it on thick: Recent progress in layer-by-layer (LbL) assembly is summarized to highlight the development of this approach from simple self-assembly to nanoarchitectonics. Advances in LbL research are categorized according to physical, chemical, and biological innovations. The fabrication of hierarchical structures and examples of LbL assemblies with graphene oxide are also described.



Katsuhiko Ariga,* Eungjin Ahn,
Minju Park, Byeong-Su Kim*



**Layer-by-Layer Assembly: Recent
Progress from Layered Assemblies to
Layered Nanoarchitectonics**