Layer-by-layer assembly as a versatile bottom-up nanofabrication technique for exploratory research and realistic application

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The layer-by-layer (LbL) adsorption technique offers an easy and inexpensive process for multilayer formation and allows a variety of materials to be incorporated within the film structures. Therefore, the LbL assembly method can be regarded as a versatile bottom-up nanofabrication technique. Research fields concerned with LbL assembly have developed rapidly but some important physicochemical aspects remain uninvestigated. In this review, we will introduce several examples from physicochemical investigations regarding the basics of this method to advanced research aimed at practical applications. These are selected mostly from recent reports and should stimulate many physical chemists and chemical physicists in the further development of LbL assembly. In order to further understand the mechanism of the LbL assembly process, theoretical work, including thermodynamics calculations, has been conducted. Additionally, the use of molecular dynamics simulation has been proposed. Recently, many kinds of physicochemical molecular interactions, including hydrogen bonding, charge transfer interactions, and stereo-complex formation, have been used. The combination of the LbL method with other fabrication techniques such as spin-coating, spraying, and photolithography has also been extensively researched. These improvements have enabled preparation of LbL films composed of various materials contained in well-designed nanostructures. The resulting structures can be used to investigate basic physicochemical phenomena where relative distances between interacting groups is of great importance. Similarly, LbL structures prepared by such advanced techniques are used widely for development of functional systems for physical applications from photovoltaic devices and field effect transistors to biochemical applications including nano-sized reactors and drug delivery systems.

I. Introduction: basics of LbL

A revolution in our daily lifestyles has been brought about by the widespread introduction of miniaturized devices such as cellular phones and mobile computers, which are reliant on silicon-based nanotechnology and sophisticated 'top-down' type fabrication techniques. However, this solid state technology is expected to encounter fabrication size limitations so that the more novel 'bottom-up' type nanofabrication has been recently paid attention as an alternative manufacturing strategy. Bottom-up nanofabrication is driven by the self-assembling processes of component molecules, where various examples based on supramolecular chemistry have been intensively investigated.[1–15] Several of these are related to fabrication of ultrathin films[16–27] because thin film preparation on certain surfaces is an important subject in connection with functional nanomaterials and artificial devices such as electrodes and transistors.

Various strategies for ultrathin film preparation have been employed widely such as the Langmuir-Blodgett (LB) technique[28–35] and the self-assembled monolayer (SAM) method.[36–40] Unfortunately, these approaches are not always useful for practical application. The LB method is an elegant way to build-up multilayer structures, although it suffers from the requirement for rather expensive instruments and it is not applicable for many kinds of non-amphiphilic material. The SAM technique can be applied to a wider range of substances, but it is not a useful method for multilayer fabrication. Compared to these traditional strategies, the layer-by-layer (LbL) adsorption technique is an easy and inexpensive process for multilayer formation and allows different types of materials to be incorporated in the film structures.[40–45] Therefore, the LbL assembly can be regarded as a versatile bottom-up nanofabrication technique.

Some time after the suggestive report by Iler,[46] the LbL assembly was first realized and established by Decher and coworkers.[47–50] Subsequently, a great number of reports concerning LbL films preparation using various techniques have been published. As an outline of the technique, LbL assembly is mainly conducted through electrostatic interaction, as illustrated in Fig. 1. Relatively high concentrations of the substances in solution lead to excess adsorption of the substances, *i.e.*, charge neutralization and resaturation lead to charge reversal, which was proved by Bernt *et al.* through a direct surface force measurement.[51] Alternation of the surface charge

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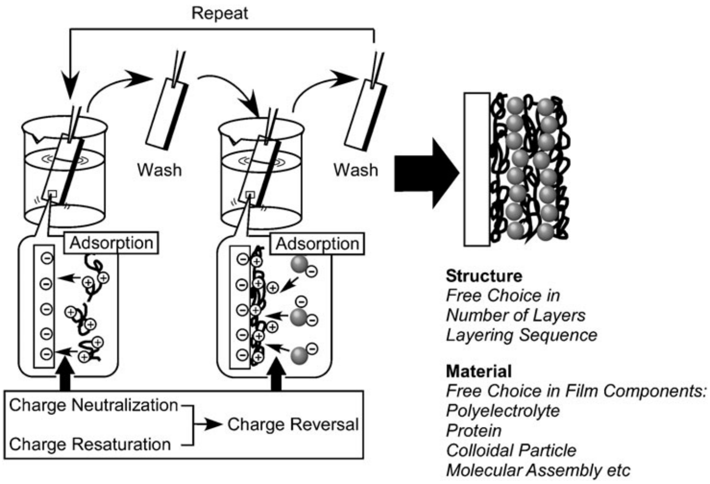

Fig. 1 Outline of LbL assembly through electrostatic interaction.

results in a continuous assembly between positively and negatively charged materials affording a great freedom in the number of layers and layering sequence.

One of the most prominent advantages of the LbL assembly is its simplicity and low cost—beakers and tweezers are the only apparatus required. The variability of the applicable materials is another of the most pronounced advantages of this method. In addition to conventional polyelectrolytes[52–57] such as poly(allylamine hydrochloride) (PAH), poly(diallyldimethylammonium chloride) (PDDA), and poly(ethyleneimine) (PEI), poly(sodium styrenesulfonate) (PSS), poly (sodium vinylsulfonate) (PVS), and poly(acrylic acid) (PAA) as anionic species, various functional polyelectrolytes have been assembled including, poly(*p*-phenylenevinylene) (PPV) for light-emitting diodes,[58,59] azobenzene-containing polycation and polyanion for non-linear optics,[60] and poly(amidoamine)dendrimer (PAMAM) and its metal composites.[61,62] Because most biomaterials, especially water-soluble proteins, have charged sites on their surface, they are generally assembled by electrostatic LbL adsorption as demonstrated when assembling films of proteins,[63–74] DNA,[75–83] and charged polysaccharides.[84–90] As a remarkable example, alternate assembly between charged virus and polyelectrolyte was demonstrated by Lvov *et al.*[91] Charged inorganic substances, including colloidal nanoparticles,[92–105] clay,[106–108] nanosheets,[109–117] modified zeolite crystals,[118] two-dimensional perovskite,[119] and polyoxometalates[120–122] have also been used for LbL assembly. Not limited to polymeric materials, charged supramolecular assemblies such as bolaamphiphile monolayers,[122–124] lipid bilayers,[125,126] LB films,[127] and stacked dye molecules[128–141] have been demonstrated to be converted into LbL films.

A broad freedom in the LbL films' structure allows us to fabricate higher dimensional structures from functional components. One of the most outstanding strategy modifications for LbL assembly preparation involves invisible particles and subsequent hollow capsule formation, and was amongst pioneering work reported by Möhwald, Caruso, and coworkers (Fig. 2A).[142,143] In this strategy, the LbL films were assembled sequentially, similarly to the conventional assemblies, on a colloidal core. Dissolution of the central particle core upon exposure of the particles to appropriate solvents results in hollow capsules. The hollow capsules obtained can be used for various purposes[144–160] including encapsulation of guest substances and controlled release because permeability through the sphere skin is controllable using several factors. Functional nano-sized systems can be constructed upon discerning selection of core materials. For example, polyelectrolyte wrapping

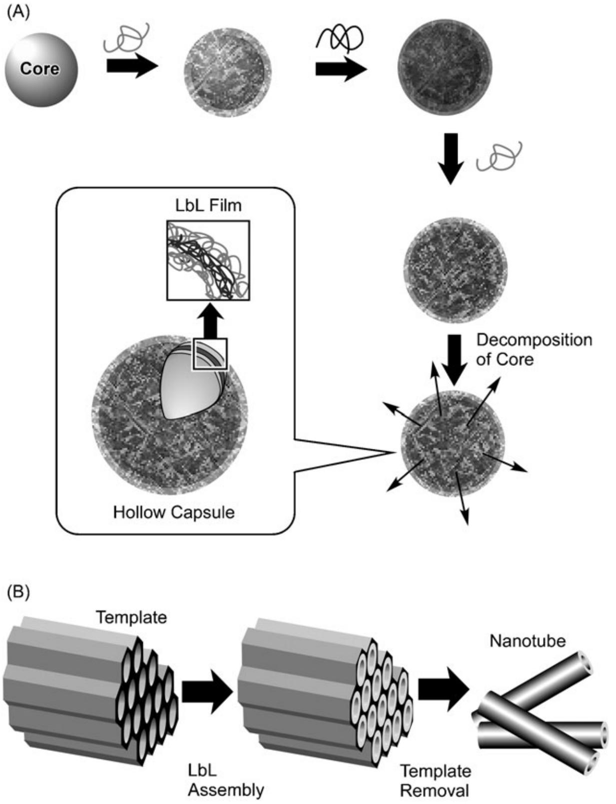

Fig. 2 Modified LbL methods for preparation of three-dimensional micro- and nanostructures: (A) LbL assembly on particle template and hollow capsule formation; (B) nanotube synthesis through LbL assembly using porous templates.

by the LbL assembly can be conducted on enzyme crystals.[161] Dissolution of the enzyme crystals giving dissolved enzymes ultimately leads to an extremely high enzyme loading in a nano-sized capsule. A similar template synthesis was applied to nanotube synthesis as illustrated in Fig. 2B.[162–166] For example, Martin and coworkers reported fabrication of nanotubes using LbL assembly between 1,10-decanediyl-bis (phosphonic acid) and zirconium ion on porous alumina template.[167] Dissolution of the alumina template results in formation of nanotube structures with outside diameters equivalent to the pore diameter of the template.

The preliminary explanation of the LbL technique illustrates the great flexibility inherent in this method of film construction. Although the LbL technology remains under development, the method already assures fabrication of nanostructures with positioning of target materials in desired geometries. The ease of this method stimulates researchers in various fundamental fields including chemistry, physics, and biology and attracts those working in practical applications including nanotechnology, materials technology, and biomedical fields. The research fields concerned with LbL assembly have developed rapidly but may have left some important physicochemical aspects unresolved. In this review, we will introduce various examples, from physicochemical investigations on the basics of this method to advanced research aimed at practical application. With this review, we would like to stimulate many physical chemists and chemical physicists to further the development of LbL assembly methods.

II. Advances in understanding of the assembly process

Although the LbL strategy requires only simple procedures, its assembling mechanism is still not fully understood. Experienced LbL researchers know that film structures and qualities depend substantially on experimental conditions. For example, Lvov *et al.* reported systematic *in situ* analyses on LbL film quality using a quartz crystal microbalance (QCM) as a sensitive mass-detection device,[168] where adsorption kinetics, drying processes, and intermediate washing were investigated systematically. Drying at each step increased the thickness of adsorbed films due to enhanced surface roughness of the films so that frequent drying is not advantageous for preparation of films of good quality. In contrast, water washing between the consecutive adsorptions was effective for successful alternate adsorption. About 10% of an adsorbed polyelectrolyte layer was removed by 5-min water washing probably due to removal of the loosely-attached materials. Shiratori and Rubner also investigated minutely film structures including the thicknesses and interpenetration depths of LbL films composed of weak polyelectrolytes, PAA and PAH, pointing out the crucial importance of pH control.[169,170] Dramatically different polymer adsorption behavior was observed as one systematically increases (or decreases) the charge density of a weak polyelectrolyte including transitions from very thick adsorbed layers (*ca.* 8 nm) to very thin adsorbed layers (*ca.* 0.4 nm) over a very narrow pH range.

In addition to these well-known features, further analyses and considerations have been made for understanding the LbL assembly mechanism. Sukhishvili *et al.* reviewed existing knowledge and summarized the relationship between polyelectrolyte multilayer growth and phase behavior of polyelectrolyte complexes in solution for rational prediction and control of deposition of a wide range of charged polyelectrolytes at surfaces.[171] Effects of a number of parameters, such as the type of interacting polyelectrolyte chains, the ratio of their lengths, and ionic strength and pH of deposition solutions, on the multilayer stability or erosion were considered, indicating that the trends observed for multilayers directly reflect the properties of polyelectrolyte complexes in solution. Several researchers have made thermodynamic considerations on the LbL assembly processes. Polyelectrolyte association is fundamentally an ion exchange process, where polymer-counterion associations are replaced by polymer–polymer ion pairs. The pairing of oppositely charged polyelectrolyte segments could appear to be driven by strongly exothermic mixing, through multiple, cooperative, and specific electrostatic interactions. However, Schlenoff and coworkers revealed, by using highly sensitive analyses such as isothermal calorimetry titration, that the polyelectrolyte association was driven largely by entropy, that is, by the release of counterions and waters of hydration from the dissolved polyelectrolyte chains.[172] The association constant for complex formation showed little temperature dependence, confirming the ideal nature of complexation. Haynie and coworkers investigated polyelectrolyte complex formation between PSS and PAH over a range of ionic strengths using isothermal titration calorimetry and similarly proved an entropy-driven nature of complex formation.[173] The thermodynamic parameters suggest the formation of different types of complexes and aggregates due to salt-induced conformational changes in the polyelectrolyte conformation, as described in terms of changes in the Debye screening length of the polyelectrolytes. Although salt-free conditions induced formation of insoluble, charge-compensated complexes with defined stoichiometry, the formation of a soluble nonstoichiometric complex is favored. Remaining charges make the polyelectrolyte complexes soluble, limiting the extent of polyelectrolyte assembly on a substrate in the LbL process. Increases in salt concentration force the polyelectrolytes to contract and form compact globules of reduced net charge, resulting in enhanced LbL assembly. Caruso and coworkers investigated the influence of the linear charge density of a polyelectrolyte chain on the formation of multilayers, using random copolymers of varying charge density, and revealed that synergistic nonelectrostatic interactions allow the growth of multilayers with polyelectrolytes of a very low charge density.[174] The significant differences in the surface roughness and packing density of the films with copolymers of different charge densities would be of interest for permeability and elasticity studies.

Effects of external factors on the LbL assemblies are also topics for physicochemical consideration. The amount of flexible polyelectrolyte deposited onto a surface depends to a great extent not only on the ionic strength but also on coexisting electrolyte species. Salomäki *et al.* found out that the thickness of thin dry LbL films of PSS and PDDA follows reasonably well the position of the counteranion in the Hofmeister series.[175] The Hofmeister series[176,177] goes as follows:

$ClO_4^- > SCN^- > I^- > NO_3^- > Br^- > Cl^- > CH_3COO^- > HCOO^- > F^- > OH^- > HPO_4^{2-} > SO_4^{2-}$. The anions on the left of chloride in the abovementioned series are chaotropic and exhibit weaker interactions with water than water itself. On the other hand, the ions on the right of chloride are cosmotropic exhibiting strong interactions with water. The hydration entropy and viscosity parameter of the anions have a strong relation to the thickness of the dry multilayer. The chaotropic anions apparently screen strongly the polyelectrolyte charges inducing the deposition of polyelectrolyte in a loopy conformation onto a surface, resulting in a thick layer. Strong binding of these anions with limited hydration also leads to the lowest viscosity as a result of shrinking of the polyelectrolyte, yielding a thick polyelectrolyte layer. In contrast, the cosmotropic anions do not screen charges, allowing the polyelectrolyte to deposit in a more planar form. The same research group reported studies on the effect of temperature in LbL assemblies of PDDA/PSS and PAH/PSS.[178] The increase of temperature in the LbL deposition process was shown to have a considerable effect on the rate of the LbL assembly, which is different for the cases of PDDA/PSS and PAH/PSS assemblies. Increasing temperature generally leads to extension of the exponential growth regime as compared with the linear one.

Deposition of materials in the LbL assembly is not always uniform. Kotov and coworkers reported detailed observations of the surface structures of assembled films of yttrium iron garnet nanoparticles (YIG) with PDDA.[179] The growth of YIG films prepared by the LbL assembly can occur *via* two deposition modes, *i.e.*, sequential adsorption of densely packed adsorption layers (normal growth mode) and in-plane growth of isolated particle domains (lateral expansion mode). The origin of the lateral growth is in the interplay of particle/particle and particle/polyelectrolyte interactions rather than in a substrate effect, which can be observed for various aqueous colloids. The latter mode should be avoided for preparation of a sophisticated layered structure. Grafting of the charged polymer on the nanoparticles significantly increases particle/polyelectrolyte and particle/particle interaction, resulting in formation of a densely packed particle layer and avoidance of the unfavorable lateral growth deposition. Deposition processes of such LbL assemblies were also theoretically simulated. Dobrynin and coworkers used molecular dynamics to simulate the LbL assemblies from flexible polyelectrolytes and rigid charged nanoparticles.[180] A better layer separation can be attained through incorporation of the nanoparticles into multilayered films, but a higher film roughness was also expected. Molecular dynamics approach was similarly conducted in polypeptide multilayers. Haynie and coworkers reported a molecular dynamics study of the physical basis of interaction between poly(L-lysine) (PLL) and poly(L-glutamic acid) (PLGA) in LbL films,[181] which could be used in a range of applications such as artificial cells, drug delivery systems, cell/tissue scaffolds, artificial viruses, and implantable device coatings. The results obtained suggest that hydrophobic interactions as well as electrostatic interactions play a significant role in PLL/PLGA LbL assemblies and that the preferred orientation of peptides in the β-sheet structures is antiparallel within sheets and parallel between sheets. Such approaches supply useful information to understand better how various types of noncovalent interactions contribute to the structure and stability of polypeptide multilayer films.

III. Development of assembly 1: novel mechanisms

The driving force of the LbL assembly is not limited to electrostatic interactions. Many kinds of physicochemical interactions have been used in the modified LbL techniques. LbL assembly based on metal–ligand interaction and/or metal coordination has a long research history comparable with that of electrostatic LbL methods. Mallouk and co-workers initiated the LbL assembly based on metal–phosphate interaction.[182–185] Hatzor *et al.* similarly developed a metal-coordination assembly for hybrid multilayer formation using bishydroxamate and phosphonate.[186] van der Boom and co-workers reported the LbL assemblies consisting of rigid-rod chromophores connected by terminal pyridine moieties to palladium centers.[187] Rubinstein and coworkers synthesized a C_3-symmetric tridentate hexahydroxamate ligand molecule that was used for coordination self-assembly of branched multi-layers on Au surfaces pre-coated with a self-assembled monolayer of ligand anchors,[188] where the branched multi-layer films display improved stiffness, as well as a unique defect self-repair capability, attributed to cross-linking in the layers and lateral expansion over defects during multilayer growth. The LbL assembly through hydrogen bonding between hydrogen-donor and hydrogen-acceptor is also possible. Hydrogen-bonded LBL films were first demonstrated by Rubner *et al.*[189,190] and later investigated by Sukhishvili *et al.*[191,192] Marks and coworkers prepared out-of-plane non-centrosymmetric microstructures by the layer-by-layer deposition from air phase (Fig. 3A).[193,194] In their design, the non-centrosymmetric layered structure was obtained through intermolecular longitudinal triple hydrogen bonding interactions, which align chromophore molecules head-to-tail and preferentially perpendicular to the substrate. Angle dependent second harmonic generation (SHG) response was detected from the obtained films. Wang and coworkers proposed a new hydrogen-bonding-based LbL method that allows the fabrication of all-conjugated polymer multilayer thin films in common organic solvents.[195] Xu, Chen and coworkers reported fabrication of composite LbL multilayer films fabricated from a spherical polymer brush with a poly(methylsilsesquioxane) core and PAA hair chains through hydrogen bonding with poly(vinylpyrrolidone) as partner components (Fig. 3B).[196] Selective dissolution (for removal of poly(methylsilsesquioxane) parts) and calcination (for removal of organic moieties) were imposed on the film to adjust its composition and optical properties. LbL assembling of dye molecules without use of polyelectrolyte components was realized by Webber and co-workers,[197] who assembled perylene diimides carrying four positive or negative charges with the aid of strong π–π interaction. The strongly quenched fluorescence is evidence for π stacking, and the dependence of the fluorescence intensity on the outermost layer suggests efficient energy transfer between perylene diimide moieties.

Introduction of covalent bonding to the LbL technique would significantly strengthen the assembly structure, which

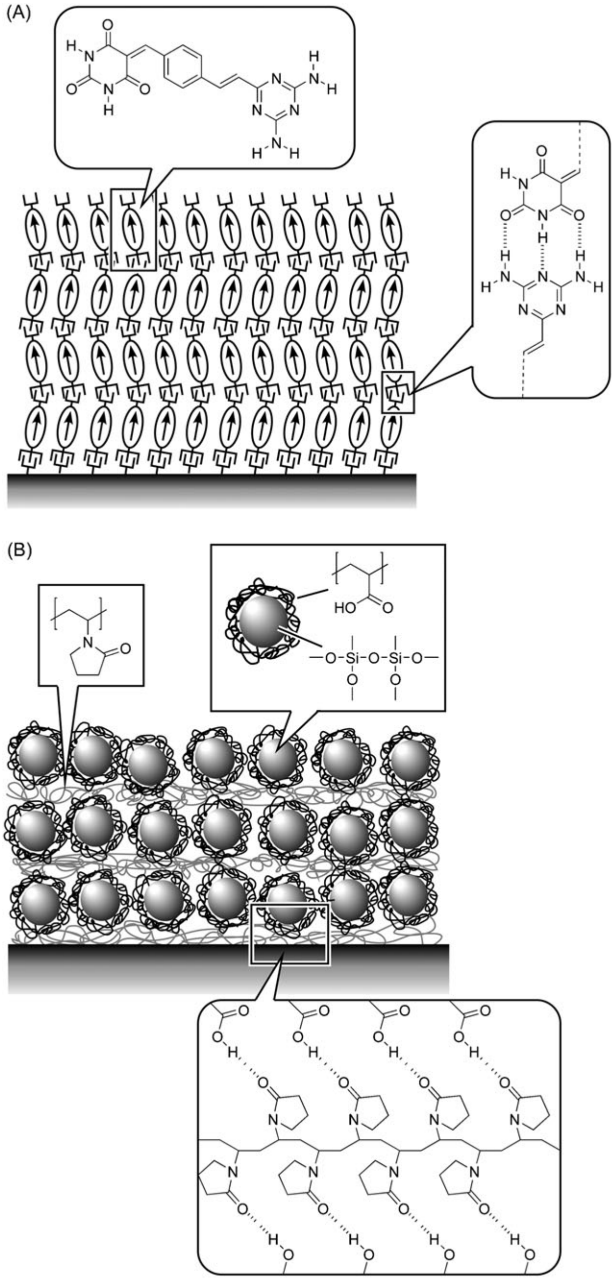

Fig. 3 LbL assembly through hydrogen bonding; (A) formation of non-centrosymmetric layers; (B) hydrogen bonded assembly between polymer brush and linear chain. Reprinted with permission from ref. 194, S. Keinan *et al.*, *Chem. Mater.*, 2004, **16**, 1848. ©2004, American Chemical Society and from ref. 196, S. Yang *et al.*, *Langmuir*, 2006, **22**, 338. ©2006, American Chemical Society.

is highly advantageous for practical application. Cao and coworkers reported fabrication of LbL films using a nitro-containing diazoresin (NDR) formed from 2-nitro-*N*-methyl-diphenylamine-4-diazonium salt (NMDS) with formaldehyde as polycation and PSS as polyanion.[198] Upon UV-irradiation and following the decomposition of the diazonium group, a covalent bond forms between the layers, the multilayer films become more stable and more resistant to etching by organic solvents or solutions. Kohli and Blanchard reported on the covalent layer-by-layer growth of multilayers of diphenylmethane derivatives where interlayer bonding is through a urea moiety.[199] Caruso and coworkers introduced click chemistry for LbL assembly (Fig. 4A).[200] The LbL assembly was performed by sequentially exposing the substrates to poly (acrylic acid) with either azide and alkyne functionality solutions containing copper sulfate, finally providing covalently linked ultrathin films with designed structures. Li and coworkers presented a method to fabricate complex nanotubes of PEI and 3,4,9,10-perylenetetracarboxyldianhydride through alternate deposition and covalent bond formation (Fig. 4B).[201] The electrooptical properties of the small molecule are retained after the wall assembly, rendering the nanotubes fluorescent. The obtained nanotubes may have potential applications in catalysis or drug delivery and the design of optical devices and sensors.

Various interactions including biochemical and physicochemical forces have been used widely for the LbL method. Some biomaterials are capable of recognizing and binding their substrates with incredibly high efficiency and selectivity, and this can be utilized as a driving force for LbL assembly.[202–207] Kunitake and coworkers reported assemblies of rectin, concanavalin A with polysaccharides, glycogen (branched polyglucose).[208] Recently, Anzai and coworkers demonstrated that the LbL films of concanavalin A and glycogen can be disintegrated upon exposure to sugars in aqueous solution at neutral pH upon addition of free sugars as competitors to the binding sites of concanavalin-A.[209] A well-investigated biospecific interaction, the biotin-avidin system, can also be applied to the LbL assembly.[210,211] As use of physical interaction in the LbL assembly, Ito and coworkers introduced use of charge transfer interactions for LbL assembly by demonstrating assemblies between an electron-accepting polymer [poly(2-((3,5-dinitrobenzoyl)oxy)ethylene methacrylate] and an electron-donating polymer [poly(2-(9-carbazoyl)ethyl methacrylate].[212,213] They also reported nonlinear optical properties of similarly assembled films by copolymerization of a nonlinear optical dye with donor polymer.[214] Akashi, Serizawa, and co-workers reported alternate LbL assembly of syndiotactic hydrophobic poly(methyl methacrylate) (PMMA) and its isotactic counterpart through alternate repetition of physical adsorption and stereocomplexation.[215–218] The same research group extended this technique to prepare artificial enzymes.[219,220] LbL films of a stereocomplex between isotactic-PMMA and syndiotactic-poly (methacrylic acid) (PMAA) with a 1 : 1 unit-molar stoichiometry was first prepared, followed by selective dissolution of one of them, resulting in porous syndiotactic-PMAA or isotactic-PMMA films. The macromolecular nanospaces in the resulting films could be used in stereoregular template polymerization of isotactic-PMMA and syndiotactic-PMAA, respectively. Ikeda, Shinkai, and coworkers reported preparation of multilayer films comprised of C_{60} fullerene and porphyrin layers using the LbL method based on a homohexacalix[3]arene-[60] fullerene 2 : 1 supramolecular complex formation.[221] Photocurrent measurements were carried out of these layers deposited on the modified ITO electrode in a 0.1 M Na_2SO_4 solution containing 50 mM of ascorbic acid as a sacrificial electron donor, demonstrating a

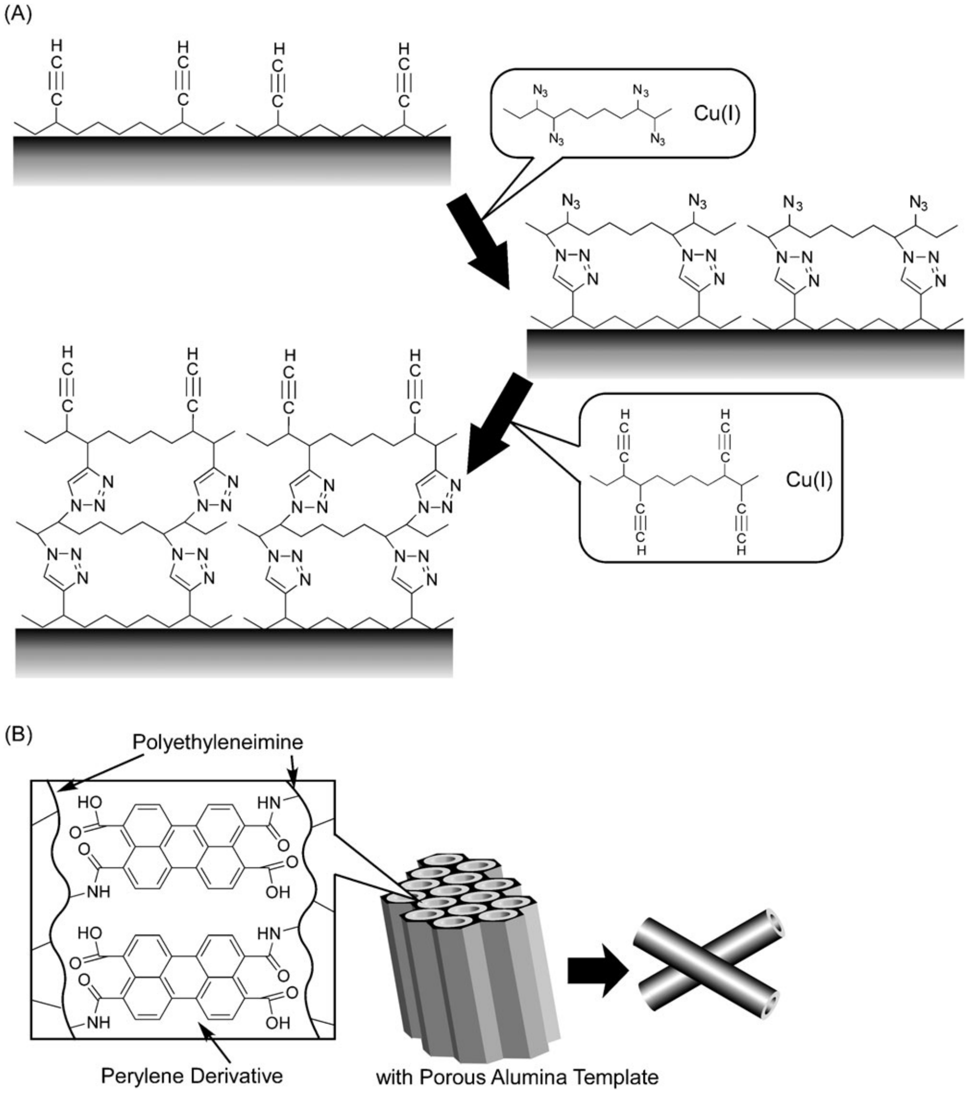

Fig. 4 LbL assembly through covalent bond formation; (A) LbL assembly based on Click chemistry; (B) nanotube synthesis through covalent-bond-based LbL assembly. Reprint with permission from ref. 200, G. K. Such *et al.*, *J. Am. Chem. Soc.*, 2006, **128**, 9318. ©2006, American Chemical Society and from ref. 201, Y. Tian *et al.*, *Langmuir*, 2006, **22**, 360. ©2006, American Chemical Society.

photocurrent flow from porphyrin units through C_{60} units to electrode. Huskens and coworkers reported LbL multilayers based on multivalent supramolecular interactions between guest-functionalized dendrimers and cyclodextrin-modified gold nanoparticles.[222] Step-wise sol-gel reaction at the surface of a solid support was also used for LbL assembly of metal oxide layer as reported by Kunitake and co-workers.[223–225] This surface sol-gel method with titanium butoxide was conducted in the presence of an azobenzene derivative guest, and the resulting film after the guest removal was used for molecular imprinting type recognition.

IV. Development of assembly 2: technical advances

Procedures for LbL assembly are relatively simple, so that there is plenty of scope for technical improvement. For example, the procedure can be automated.[226] Shiratori and coworkers developed an automated LbL film assembler by combining with a mass-controlled mechanism.[227–229] A solid plate was attached to the arm of a robot together with QCM as sensitive mass detector, which provided frequency shifts during adsorption of the materials. Feeding back the data acquired by the QCM from the deposition to the dipping time allowed preparation of a high quality self-assembly film. As a result, the layer thickness of the films can be controlled with nm-order accuracy. The cross-sectional transmission electron microscopy (TEM) observation of the films formed by the conventional time controlled dipping method and the newly established mass-controlled dipping method revealed that the interface of the hetero structure of the latter was much smoother than the former. The remarkable advantage of the mass-controlled dipping method was also proved by *in situ* observation of the adsorption process of the polyelectrolytes in solution using an atomic force microscopy (AFM).

Combination of the LbL methods with other techniques for thin film preparation has been also conducted resulting in technical improvements. In the LbL adsorption process, charged polyelectrolyte chains are adsorbed onto an oppositely charged surface due to the electrostatic attraction. This can be regarded as a self-diffusion process. Therefore, the process needs extra time inducing significant adsorption of the weakly-attached polyelectrolyte chains giving increased surface roughand poor film quality. The spin-coating technique has also been combined with LbL assembly.[230–232] For example, Char and coworkers reported a spin-coating LbL assembly method as an alternative for making well-organized multilayer films in a very short process time (Fig. 5A).[233] This method has several technical advantages when compared with conventional dipping procedure. In the case of the conventional dipping process, polyelectrolyte chains are allowed to diffuse toward the substrate according to the self-diffusion process. In contrast, for the spin-coating process the adsorption and rearrangement of adsorbed chains on the surface and the elimination of weakly bound polymer chains from the substrate are achieved almost simultaneously at a high rate of rotation over a short time period. The molar concentration of the polyelectrolyte solution during the short deposition time is significantly increased upon rapid elimination of water during the spinning process, yielding thick layers, despite the thin film formation typically provided by the centrifugal force and air shear force. This spin-coating LbL process yields a highly ordered internal structure far superior to the structure obtained with the conventional dipping method probably due to a mechanical effect upon the air shear force caused by the spinning process. Johal, Wang, and coworkers reported the application of spin-coating LbL assembly to a variety of polyelectrolytes, including polymers and dendrimers.[234,235] Preparation of single-species thin films through multiple deposition cycles of the same polyelectrolyte was also demonstrated. They proposed that the use of alternating charges is not an absolute requirement when building polyelectrolyte multi-layered films by spin-coating LbL assembly.

Combination of the LbL method and the spraying technique has been reported.[236,237] For example, Decher and coworkers proposed preparation of polyelectrolyte film by successive spraying of polycation and polyanion solutions (Fig. 5B),[238] and the films prepared according to this concept, from PSS and PAH, were compared with those prepared by the classic dipping LbL assembly. The influences of various parameters such as spraying time, polyelectrolyte concentration, and effect of film drying during multilayer construction were examined. The thickness of the multilayers increased linearly with the number of deposition cycles. The LbL assembly of films is very fast and leads to films with low surface roughness as estimated by AFM and X-ray reflectometry. Spray deposition allows regular multilayer growth even under conditions for which dipping fails to produce homogeneous films, such as extremely short contact times. Drainage constantly removes a certain quantity of the excess material arriving at the surface, and the rinsing step can be eliminated, resulting even further improvements in preparation times for the whole film construction process. Fery and coworkers also used the spray LbL technique for assembly of inorganic/organic nanocomposite multilayered films consisting of Au

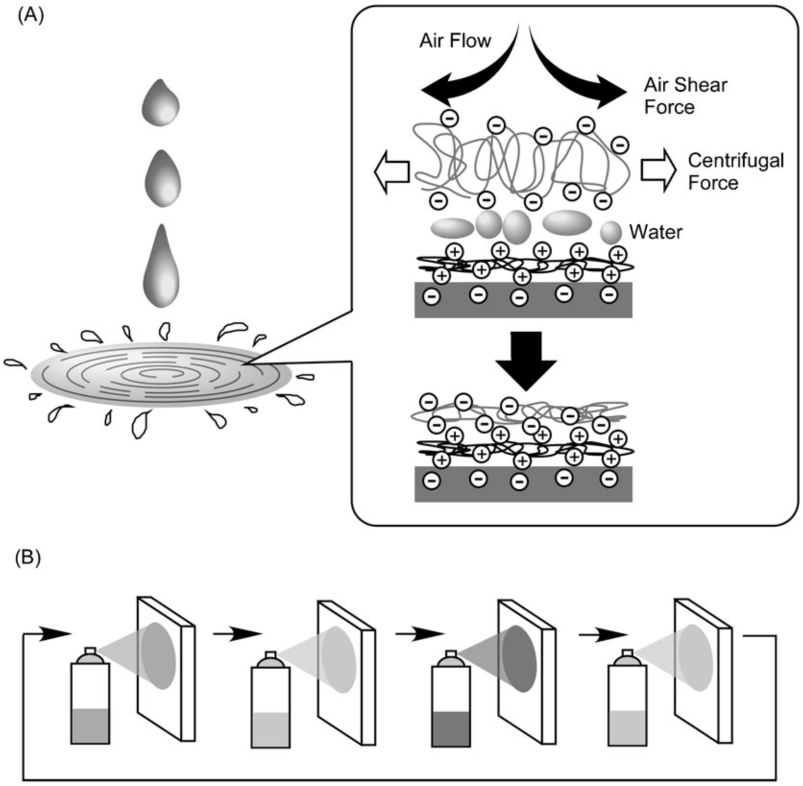

Fig. 5 Advanced techniques for LbL assembly; (A) spin-coating LbL assembly; (B) spraying LbL assembly. Reprint with permission from ref. 237, A. Izquierdo *et al.*, *Langmuir*, 2005, **21**, 7558. ©2005, American Chemical Society.

nanoparticles and photosensitive polycation nitrodiazoresin.[239] UV irradiation of the films leads to the formation of covalently cross-linked composites with an improved chemical stability, greatly broadening the flexible processing and the application field of the resultant functional films. The buckling test shows that the nanostructures of the composite films such as the identity of the organic matrix and the amount of inorganic nanoparticles are essential for variation of the mechanical properties.

Applying etching processes to the LbL techniques are useful in the preparation of nano-sized object with sophisticated structures. For example, Caruso and coworkers reported fabrication of nanoporous polymer films with controlled pore size upon partial etching of nanoparticle/polyelectrolyte composite precursor films (Fig. 6A).[240] The nanoparticle-polyelectrolyte hybrid multilayers ((SiO_2 nanoparticle/PAA)/PAH) can be assembled by the alternate LbL adsorption from a blend of colloidal silica particles and PAA, with PAH. After cross-linking of the films, the SiO_2 nanoparticles were removed by dissolution with ammonium fluoride-buffered hydrofluoric acid (HF/NH_4F). The permeability of the films after silica particle removal increased, as demonstrated by an increased amount of protein (BSA) adsorbed with increasing bilayer number. The proposed method provides a general approach for fabricating polymer thin films with controlled pore sizes. Preparation of free-standing LbL film was achieved by elective etching of the substrate surface, as reported by Mamedov and Kotov.[241] They prepared LbL films on a cellulose acetate layer, which was selectively dissolved providing self-standing LbL films. Tsukruk and coworkers used this strategy for fabrication of freely suspended, multi-layered nanocomposite membranes containing gold nanoparticles (Fig. 6B).[242–245] The gold nanoparticles were deposited alternately with oppositely charged polyelectrolytes on solid supports covered with a sacrificial layer of cellulose acetate, followed by coverage with additional assemblies of conventional polyelectrolytes. The multi-layered polymer films with gold nanoparticles were released from the supporting silicon wafer by dissolving the sacrificial cellulose acetate layer in acetone. The obtained films possess very stable micromechanical characteristics and a sensitivity far surpassing any existing pressure sensors. Hammond and coworkers similarly demonstrated preparation of free-standing films of poly(ethylene oxide) (PEO) and PAA which interact with each other through hydrogen bonding.[246] The crystallization of PEO is fully suppressed in these composite assemblies, which proves advantageous for applications such as ultrathin hydrogels, membranes, and solid-state polymer electrolytes.

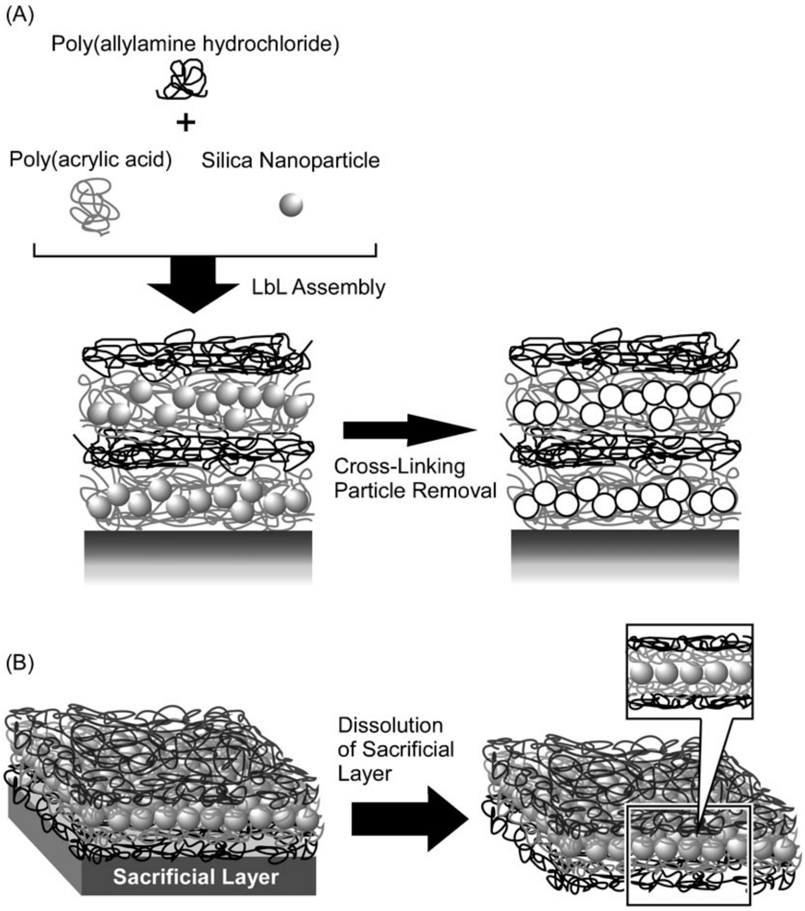

Fig. 6 Etching processes on the LbL films; (A) formation of nanoporous structure; (B) preparation of free-standing film. Reprint with permission from ref. 240, Q. Li *et al.*, *Chem. Mater.*, 2006, **18**, 5480. ©2006, American Chemical Society.

V. Development of assembly 3: new components

The simplicity of LbL assembly also permits utilization of an enormous library of molecular or polymeric components and this library is being expanded continuously. In particular, assemblies of functional elements such as supramolecular objects and nanomaterials have been investigated. For example, LbL assemblies of micelles were reported by several research groups.[247–249] Zhao and coworkers realized the LbL assembly of two different polymer micelles through alternating deposition of micelles with a polyanion and a polycation corona, poly(4-vinylpyridine)-*b*-poly(*tert*-butyl acrylate) and poly(acrylic acid)-*b*-poly(4-vinylpyridine), without the use of intermediate polyelectrolyte layers.[250] Because the micelles are capable of including hydrophobic functional molecules, this approach offers a more robust and versatile way to incorporate and organize different hydrophobic species into thin films of layered structures.

Vesicles, liposomes and their related structures were also reported as components applicable to the LbL technique. Katagiri *et al.* realized LbL assembly using a superstable organic-inorganic vesicle "cerasome".[251,252] The cerasome was prepared from the silane-bearing amphiphile [3-((*N*,*N*-dihexadecylaminosuccinyl) aminopropyl)triethoxysilane under mildly acidic conditions. Formation of a silica network at the polar headgroup upon sol-gel reaction together with spontaneous formation of a bilayer structure resulted in cell-like vesicle structures with silica network at the inner and outer surfaces.[253–256] LBL assemblies between cationic polyelectrolyte and anionic vesicles[257] as well as the LBL assemblies between the anionic cerasome and the cationic cerasome[258] were demonstrated without rupture of the vesicular structures. The latter assemblies are expected to be used as multi-cellular mimics. Schaaf and coworkers demonstrated incorporation of phospholipid vesicles in the LbL films composed of poly (glutamic-acid) (PGA) and PAH.[259] AFM imaging, QCM evaluation, and ellipsometry suggested that the vesicles remain intact when adhering on the surface. Very recently, they applied the spray LbL method to this system and again demonstrated the absence of vesicle rupture based on cyclic voltammetry evaluation on guest release.[260] They also embedded vesicle reactors in the PGA/PAH multilayers for controlled mineralization.[261] The reactors contained calcium ions as active ions in the mineralization process, spermine as an activator of crystal growth, and alkaline phosphatase as a catalyst. Exposure of the prepared films with paranitrophenyl phosphate induced the formation of calcium phosphate crystals. This research should lead to reactor multilayers with the goal of performing localized chemical reactions within confined layers. Abbott, Caruso, and coworkers prepared PSS/PAH polyelectrolyte LbL multilayers on thermotropic liquid crystalline oil-in-water emulsions and investigated the effect of the LbL formation on the orientation of the liquid crystals using polarized light microscopy.[262] A bipolar-to-radial ordering transition triggered by exposure of the LbL film-coated droplets to surfactant was observed to be slowed by 2 orders of magnitude relative to naked liquid crystalline droplets. Their successful demonstration on the LbL assembly at the mobile interfaces between liquid droplets and aqueous phases could be extended as a general method for LbL assembly on liquid templates, allowing a versatile route for producing hollow polymeric capsules.

Nanostructures including nanotubes and nanosheets have been paid much attention as functional units, and fabrication of these motifs within desired assemblies is one of the big targets in current technology. LbL assembly of these nanostructures has been conducted. In order to subject carbon nanotubes to the electrostatic LbL assembly, charged sites have to be attached to the carbon nanotube structures. Noy and coworkers introduced cationic charges to the carbon nanotube through strong interaction between nanotube surface and an aromatic pyrene derivative (Fig. 7A).[263] The modified nanotubes were sequentially wrapped using LbL methods with appropriate polyelectrolytes, providing a conductive nanowire inside an insulative coat. Wrapping carbon nanotubes with chemically active polymers is also advantageous for immobilization of functional organic elements, including proteins, in the vicinity of the nanotube. Kotov and coworkers partially oxidized the nanotube surface to introduce carboxylic groups as anionic sites, which were assembled with PEI and PSS in a layer-by-layer manner.[264] Cross-linking of the obtained LbL films significantly strengthened the film structure, yielding mechanically strong self-standing films. The same research group reported LbL

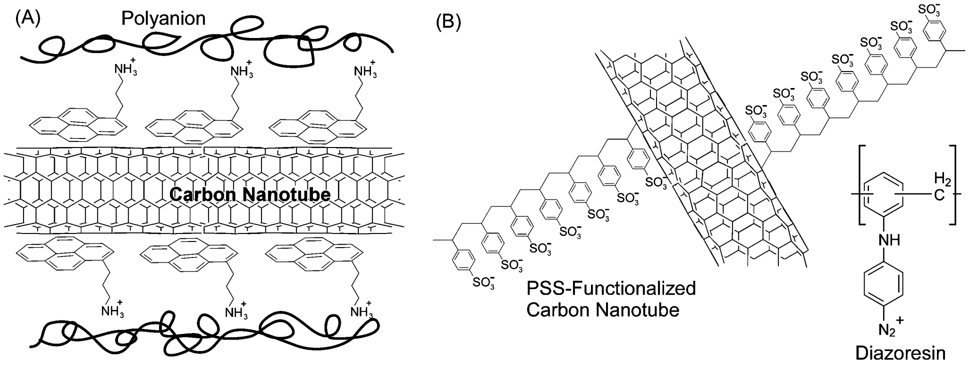

Fig. 7 Modification of carbon nanotube with LbL assembly; (A) wrapping of carbon nanotube upon LbL assembly through interaction with pyrene derivative; (B) components for covalently linked LbL assembly between carbon nanotube and polymer. Reprint with permission from ref. 263, A. B. Artyukhini *et al.*, *Langmuir*, 2004, **20**, 1442. ©2004, American Chemical Society.

assembly between PSS-modified carbon nanotube and diazoresin (Fig. 7B).[265] All covalently conjugated films were obtained after the cross-linking process. Sasaki and coworkers have extensively researched the LbL assembly of inorganic nanosheets and nanotubes to explore novel photoelectronic properties in nanosized structures. They reported preparation of the LbL films of titanate nanotubes, Ag- or Au-loaded nanotubes, and nanotube/nanosheet heterocomposites, with PDDA as counterionic partner.[266] This process may be explored for custom synthesis of titanate nanotube-based multicomponent and multifunction ultrathin films for various applications in photocatalysis, solar energy conversion, and electrochromic and self-cleaning devices.

VI. Advanced analyses and novel properties

Analytical methods that are applicable to other thin films can generally be used for evaluation of the LbL assembled films. Regular film growth can be detected by UV-Vis and FT-IR spectroscopies if the adsorbed materials have specific absorption bands. More generally, the thickness of the adsorbed layers can be evaluated by X-ray reflectivity, surface plasmon resonance (SPR), and scanning angle reflectometry (SAR) and film mass can be quantified by QCM with precision at the nanogram-level. The morphology of the films can also be analyzed by various microscopies including scanning electron microscopy (SEM), transmission electron microscopy, and scanning probe microscopies (SPMs). Not limited to these fundamental analyses, various analytical tools have been used in LbL science and technology. Because the LbL method provides ideal layered films from various functional molecules, the LbL structures provide media appropriate for investigation of physicochemical phenomena using sophisticated analytical techniques, which is also useful for a better understanding of the mechanism of formation of LbL films.

LbL thin films incorporating metallic nanoparticles have been examined for their use as substrates for surface-enhanced Raman scattering (SERS), which is a phenomenon involving large increases in Raman scattering cross sections of molecules adsorbed at the surfaces of nanometer-scale metallic particles. Aroca and coworkers reported that LbL films prepared from dendrimer and colloidal Ag particles could be excellent substrates for SERS measurements, demonstrating significant enhancement capability.[267] Large electromagnetic enhancement of Raman scattering signals was found to be strongly dependent on interparticle coupling between neighboring metallic nanoparticles. Electromagnetic enhancement was still possible at distances within LbL structures although its intensity decreased as film thickness increased. Therefore these films would be useful for developing sensors with external layers that are chemically selective for specific analytes. Other optical properties of metallic nanoparticle can be tuned through modification of LbL structures incorporating the target nanoparticles. For example, the surface plasmon resonance (SPR) peak can be tuned over a wide range of wavelengths upon changing the environment and the level of the nanoparticle aggregation. Tsukruk and coworkers prepared multilayered films containing gold nanoparticles and PAH by spin-coating LbL assembly and examined the relationship between their microstructure and the corresponding SPR optical response.[268] All the films prepared showed a strong extinction peak in the region of 510–550 nm, which is due to the plasmon resonance of the individual gold nanoparticles red-shifted because of a local dielectric environment. The second strong peak was consistently observed between 620 and 660 nm, which is the collective plasmon resonance from intralayer interparticle coupling in sufficiently dense-packed films. They also proposed film designs for interlayer interparticle resonance at 800 nm. Such control of SPR signals of independent and concurrent individual, intralayer, and interlayer resonances could be critical for sensing applications.

Because the soft and flexible nature of the LbL films is compatible with biological components, incorporation of biomaterials in LbL films and their resulting functions have been researched widely. In order to use the LbL materials in practical biological applications, the preparation of LbL structures with rather complicated compositions is often required. Ferreyra, Teijelo, and coworkers prepared bioelectrodes composed of LbL films from an anionic alkaline phosphatase (AP)-polyphenol oxidase (PPO) mixture and the polycation PDDA on top of a glassy carbon electrode modified with an immunological layer.[269] They analyzed structural data obtained from these complex structures, including film thickness, the film optical properties, and the ellipsometric mass values assessed from the two models, three-layer film and reorganization layer. Combination of several analytical methods is sometimes necessary to characterize biological LbL films. Elofsson, and coworkers analyzed structures of PGA/PLL LbL films immobilized with matrix derivate protein using the combined analyses of *in situ* ellipsometry, quartz crystal microbalance with dissipation (QCM-D), and dual-polarization interferometry (DPI).[270] The latter is a relatively new technique used to measure changes in both the thickness and the refractive index of adsorbed layers *in situ*. The process of adsorption to the surface affects the evanescent field emitted from the sensing waveguide in the index of refraction resulting in changes of the light propagating through the sensing waveguide relative to the light traveling through the reference. The resulting difference is reflected as a shift in the fringe pattern in the far field, which is alternately and continuously recorded for both horizontally and vertically polarized light. By combining the results from both polarizations, a unique solution for the thickness and the refractive index can be obtained. Upon systematic comparison, an excellent agreement was found between the masses detected by ellipsometry and DPI. In contrast, the QCM-D registers a significantly larger mass, probably because of incorporation of contributions from the solvent oscillating within the LbL films. Analyses of the intrinsic activity of biological components are a valuable approach. Lu and Hu prepared bioactive LbL films from natural polysaccharides chitosan (CS) and hyaluronic acid (HA) and loaded electroactive myoglobin (Mb) in the films.[271] The cyclic voltammetric (CV) peak pair of Mb $\mathrm{Fe^{III}/Fe^{II}}$ redox couple for these LbL films on pyrolytic graphite (PG) electrodes was used to investigate the loading behavior of the CS/HA films toward Mb. The CS/HA LbL films with relatively low charge density are packed loosely and easily swelled in water, leading to greater loading volumes and shorter loading time for Mb. The importance of film structure to performance with regard to biological activities was indicated.

Versatility of film construction using the LbL assembly technique is also advantageous for introduction of new physicochemical properties. Hammond and coworkers plasticized PEO/PAA films through hydrogen bonding LbL assembly, whose films exhibited ionic conductivity exceeding those of electrostatically assembled LBL films.[272] Their results suggest research routes for the evolution of these promising solid polymer electrolytes into elements appropriate for electrochemical power storage and generation applications. Katagiri *et al*. investigated the influence of UV irradiation on polyelectrolyte LbL capsules and realized structural shrinkage upon UV irradiation of the capsules formed from polyelectrolytes with UV absorbing aromatic groups.[273] UV irradiation of capsules could be used as a viable route to alter the chemical and physical properties of polyelectrolyte capsules after their formation. This strategy may be useful in environmental applications, where it could be used to modulate the release of encapsulated substances upon exposure to sunlight. Decher and coworkers used the superiority of LbL assembly for structural design to understand some fundamental photophysical phenomena.[274] They prepared the LbL films on 13-nm-diameter gold colloids to fabricate metal core-polymer shell capsules in which the fluorescent organic dyes fluorescein isothiocyanate (FITC) and lissamine rhodamine B (LISS) are situated at various distances from the gold core (Fig. 8A). The gold nanocore quenches the fluorescence of the fluorescein and lissamine dyes situated in the outer polymer layers of the core-shell nanoparticles. By systematic control of the distance between dye and metal core in the LbL structures, the fluorescence measurements give a direct method to assess the effect of the metal core on the radiative rates. Systematic photophysical investigations revealed strongly distance-dependent fluorescence quenching and that the gold nanoparticles decrease the transition probability for radiative transitions.

Study of the mechanical characteristics of LbL objects also attracts active researchers. Jaber and Schlenoff reported on the time-dependent viscoelastic response of nanoblended films of a polyelectrolyte complex.[275] A section of the polyelectrolyte LbL film was peeled off from solid support and was mounted on a moving iron galvanometer motor and a capacitance-type force transducer. The mechanical characteristics of the LbL films were measured by applying a dynamic load with a sinusoidal rate change. The polyelectrolyte LbL films provided enhancement in damping properties over the frequency range of 0.3–10 Hz, when compared with other hydrogel damping

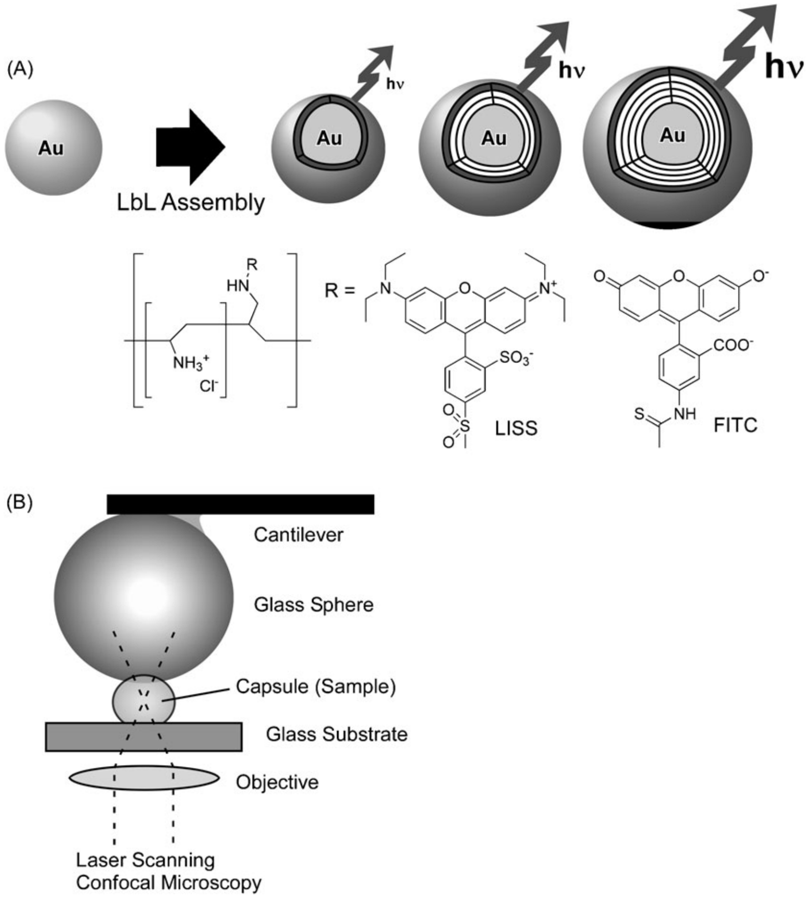

Fig. 8 Evaluation of physicochemical properties using LbL assemblies; (A) distance-dependent fluorescence quenching LbL assemblies on gold particle; (B) measurement of mechanical properties using cantilever technique. Reprint with permission from ref. 274, G. Schneider and G. Decher, *Nano Lett*., 2006, **6**, 530. ©2006, American Chemical Society and from ref. 276, B.-S. Kim *et al*., *Langmuir*, 2005, **21**, 7200. ©2005, American Chemical Society.

materials. Vinogradova and coworkers investigated the mechanical properties of dendrimer-based LbL microcapsules by measuring force-deformation curves with AFM (Fig. 8B).[276] V-shaped cantilevers attached with glass spheres were used for the force measurement, where the glass sphere was centered above the apex of a chosen capsule and deflection was dynamically imposed. Changes in the diameter of the capsule were determined optically. The dendrimer-type LbL capsules were confirmed as much softer objects than PSS/PAH microcapsules, probably because of an enhanced permeability of the polyelectrolyte/dendrimer multilayer and a resulting rapid drainage of water from the compressed microcapsules. Theoretical approaches on mechanical properties on the LbL capsules were also reported. Biesheuvel *et al.* proposed a micromechanical theory for the LbL microcapsules.[277] The model explains the essential experimental features such as a wide pH plateau in which the size remains close to the unperturbed (initial) value, the sharp increase in size at the edges of the plateau, and the fact that at the edges of the pH plateau the size increases with increasing ionic strength.

VII. Development in application 1: physical and device usages

The LbL method does not require expensive and complicated experimental apparatus or special skills and can be applied to various materials. Therefore, many kinds of applications based on the LbL technology have been proposed continuously. In the next two sections, recent application-oriented examples are introduced and are classified as (i) physical and device uses and (ii) chemical biological uses.

This LBL method offers a useful approach for fabrication of photonic devices with great accuracy in control over thickness, which is difficult to achieve by the conventional spin-coating process. It is also possible to fabricate devices with alternating layers of hole transport polymer, photosensitizer, and electron transport polymer. Kotov and coworkers fabricated photoactive LbL films from tellurium nanowires and polyelectrolyte that were found to be sensitive to light exposure.[278] A light-induced increase conductivity switched the LbL thin films between "off" and "on" states giving an optical gating phenomenon. This "light-on–light-off" cycle was demonstrated to be very stable under ambient conditions for more than 100 repetitions, with no sign of photodegradation. Kurth and coworkers developed an electrochromic device based on LbL films of polyoxometalates,[279,280] which were fabricated by the LbL deposition of Eu-polyoxometalates, PAH, and PSS on ITO-coated glass slides, and demonstrated an optical memory effect. The film was colored blue by applying a potential of ±1.8 V *versus* a reference Pt electrode, while bleaching was observed by a decrease in absorbance at 700 nm after removal of the electrical potential. It was demonstrated that this device operated reversibly with suitable response cycles. The same research group also reported that both electro- and photochromism can be combined in a single device by using the LbL film of polyoxometalate.[281] Schanze, Reynolds, and coworkers reported fabrication of photovoltaic cells using LbL films of poly(*p*-phenylene ethynylene) (PPE)-based polyelectrolyte and a fullerene derivative,[282] which exhibited moderately efficient incident monochromic photon to current conversion efficiency (IPCE) response under low-intensity monochromatic light illumination (Fig. 9A). The LbL technique permits preparation of donor–acceptor films with relatively precise (molecular level) control over the structure and energies of the active layers of photovoltaic cells. Therefore, it is possible to study the effects of features such as energy gradient driven exciton and/or charge transfer on photoconversion efficiency in organic photovoltaic cells. Chan and coworkers prepared the LbL multilayer films composed of a ruthenium terpyridine complex containing poly(*p*-phenylenevinylene) (Ru-PPV) and sulfonated polyaniline (SPAN) for photovoltaic cells that were fabricated by sandwiching the multilayer films between indium-tin-oxide and aluminum electrodes.[283] The maximum IPCE of the devices was found to be approximately 2% at 510 nm, which is consistent with the absorption maximum of the ruthenium complex. This indicates that the photosensitization process is due to the electronic excitation of the ruthenium complex. Wang and coworkers reported preparation of LbL hybrid films of conjugated polymers PPV and CdSe nanoparticles.[284] Their approach includes facile covalent crosslinking of the polymer/nanoparticle interlayers, which provides a general route for preparing robust and uniform functional thin films. A preliminary application of the hybrid films in the development of organic photovoltaics was presented. The self-assembled multilayer films exhibit steady photocurrent responses with an overall optical-to-electrical power conversion efficiency of 0.71% upon illumination with white light at 10 mW cm^{-2}.

Solar cells and fuel cells are important targets in current research, and various materials useful for these cell applications have been investigated using the LbL technique. Agrios *et al.* fabricated dye-sensitized solar cells using the LbL method.[285] A solar cell was prepared from 50-cycle layers of TiO_2 large particle on 50-cycle layers of TiO_2 nanoparticle including photo-sensitive dye N719. The upper scattering layer produced a current density of 1.8 mA cm^{-2}, accounting for 38% of the improvement due to the scattering layer over nanoparticle TiO_2. The capability to design desired film structures using the LbL techniques was emphasized in this demonstration. LbL assembly of composite polyelectrolyte multi-layer thin films offers a very effective technique for minimization of the methanol-crossover problem in direct methanol fuel cells (DMFC) as demonstrated by Jiang *et al.*[286] They proposed preparation of methanol-blocking multi-layer thin film on a Nafion membrane using LbL assembly of oppositely charged polyelectrolytes, PDDA and PSS. This LbL film on Nafion membrane showed a significant reduction in methanol crossover and on the enhancement of the performance of DMFCs. Most importantly, the LbL assembly approach appears to have a much smaller detrimental effect on the proton conductivity and chemical and thermal stabilities of the Nafion membrane, a significant advantage compared to other modification approaches.

Devices constructed with well-defined layer structures, such as field effect transistors (FET), would be appropriate targets that can benefit from LbL technology. By aiming to construct all-solid-state electrochromic device, Kim and Jung fabricated the LbL films that were constructed using poly(aniline-*N*-

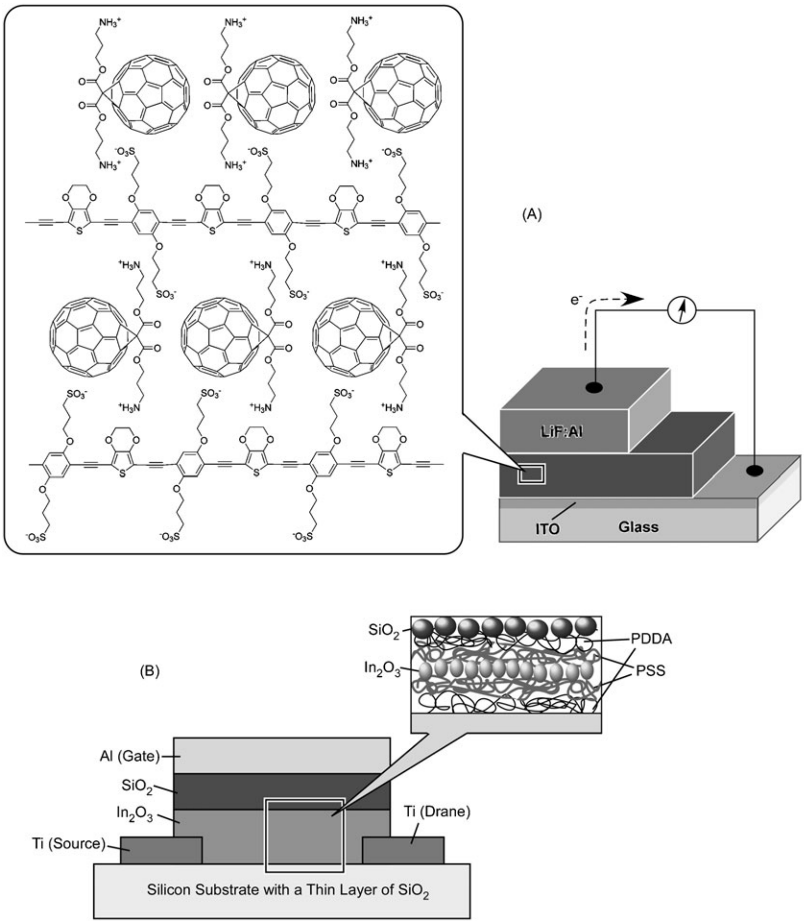

Fig. 9 Device structures based on LbL films; (A) photovoltaic cell composed of PPE and fullerene derivative; (B) FET composed of inorganic nanoparticles and polyelectrolytes. Reprint with permission from ref. 282, J. K. Mwaura *et al.*, *Langmuir*, 2005, **21**, 10119. ©2005, American Chemical Society.

butylsulfonate)s (PANBS) as an electrochromic anionic polymer, and acid-doped polyaniline (PAN) and vinylbenzyldimethyl-*n*-octadecylammonium salts (VBOD) as a polycation.[287] An all-solid-state electrochromic device based on an optimized LBL composition showed an electrochromic response at 3 V within 1 s, with a stable memory effect. Lvov and coworkers demonstrated this possibility by preparation of metal-oxide-semiconductor field effect transistor (MOSFET) arrays using the LbL process on a silicon wafer.[288] The on-off threshold voltage was 3 V and this work represents a new approach by which to fabricate low-cost MOSFETs and integrated circuits. Cui *et al.* reported fabrication of an LbL multilayer of In_2O_3 and SiO_2 nanoparticles, patterned by photolithography and lift-off methods, as channels and insulating layers, respectively, as an inorganic FET (Fig. 9B).[289] This FET worked in an accumulation mode, with a threshold voltage of -1.25 V, a carrier mobility of 4.24×10^{-3} cm^2 V^{-1} s^{-1}, and an on/off current ratio of 10^2. These approaches provide a new strategy for fabrication of low-cost micro/nanoelectronic devices and integrated circuits.

Nolte *et al.* demonstrated the use of LbL assembly and *in situ* nanoreactor chemistry for creating multilayer nanocomposites, where the concentration of a nanoparticle species can be modulated throughout the depth of the film in a desired way.[290] They produced a digitized rugate filter, a special type of dielectric mirror possessing many thin layers that approximate a continuous, periodic refractive index profile, through *in situ* growth of silver nanoparticles to selectively increase the refractive index of precisely defined regions of the LbL film. Spectroscopic results obtained from the assembled device confirm the presence of a reflection band that grows in amplitude with increasing silver incorporation, reaching a peak reflectance of 75% after five silver loading and exchange cycles. The rugate structure suppresses reflection side bands, features common to Bragg reflectors and simpler dielectric mirror designs. Murase and coworkers proposed a novel and facile preparation method for the LbL films incorporating quantum dots showing intense photoluminescence from blue to red.[291] The photoluminescence efficiencies of the quantum dots (CdTe or ZnSe, both are thioglycolic acid-stabilized) dispersed in the films were roughly half that of the initial colloidal solutions but reached 24%. The intense photoluminescence from the high quantum dot concentration with greater stability demonstrates the potential application of these multilayer quantum dot films to optical devices with full color emission. DeLongchamp and Hammond presented fabrication of a multicolored electrochromic electrode using LbL films from polycationic poly(aniline) (PANI) and a negatively ionized Prussian Blue (PB) nanoparticle.[292] Electrochemical and spectrophotometric characterization confirms the distinct and non-interacting contributions from PANI and PB and reveals that both are fully electrochemically accessible even in thick, high contrast films. Switching speed is accelerated due to the incorporation of electronically conducting PANI and the prepared nanocomposite underwent an uncolored to green to blue transition over the potential range from −0.2 to 0.6 V *vs.* K-SCE. Winnik and coworkers proposed preparation of photoluminescent oxygen sensors based upon phosphorescent platinum and palladium porphyrins and ruthenium complexes adsorbed into the pores of mesoporous silica particles at submonolayer coverage on LbL films.[293]

In one unique physical application, Cho and coworkers prepared stable superhydrophobic surfaces using LbL assembly.[294] Because the LbL method is very suitable for surface modifications, such an application would be one of the most practical ones. They prepared organic-inorganic hybrid films by LbL deposition of PAH and ZrO_2 nanoparticles coated with PAA with facile control of surface roughness and hydrophobicity. The structure of films was controlled by the number of deposition cycles using PAA-coated 100 nm ZrO_2 nanoparticles and the prelayer with PAH and PAA, yielding superhydrophobic surfaces were then successfully developed by the deposition of hydrophilic silica nanoparticles on a 10 bilayer surface of PAH/PAA-coated ZrO_2, and a simple fluorination. Moreover, the chemical stability of the film was greatly increased by heat-induced cross-linking of the film. Rubner, Cohen, and coworkers prepared hydrophilic patterns on superhydrophobic surfaces. These were created using water/2-propanol solutions of a polyelectrolyte to produce surfaces with extreme hydrophobic contrast.[295] Selective deposition of multilayer films onto the hydrophilic patterns introduces different properties to the area including superhydrophilicity. This structural design was inspired by the water harvesting wing surface of the Namib Desert beetle. Potential applications of such surfaces include water harvesting surfaces, controlled drug release coatings, open-air microchannel devices, and lab-on-chip devices. The same research group recently reported preparation of all-nanoparticle thin-film coatings that exhibit antireflective, antifogging (superhydrophilicity), and self-cleaning properties by layer-by-layer deposition of TiO_2 and SiO_2 nanoparticles.[296] The presence of nanopores in the TiO_2/SiO_2 nanoparticle coatings results in superhydrophilicity as well as antireflective properties. The superhydrophilicity of contaminated coatings could also be readily recovered and retained after ultraviolet irradiation.

VIII. Development in application 2: chemical and biological usages

The LbL films have been used in diverse areas of the chemical and biological fields including materials separation, controlled permeation and release of target materials, reactor usages, and sensing. In particular, the soft, flexible nature of the LbL films is suitable for fabrication of stimuli-responsive systems.

Selective permeation and permeation blocking are fundamental properties of membranes. A sophisticated design of the LbL films should lead to advanced properties in the corresponding fields. Hollman and Bhattacharyya prepared non-stoichiometric immobilization of charged LbL multilayers within a confined pore geometry, resulting in an enhanced volume density of ionizable groups in the membrane phase.[297] Such high density of the effective charge density permits permeation control upon Donnan exclusion of ionic species. Shiratori and coworkers fabricated LbL films from PAH and PAA, which have amino groups and carboxyl groups, respectively, on a glass filter.[298] After appropriate thermal treatment, the assembled films were subjected to filter experiments for removal of environmentally-unfriendly gasses. Basic odorants such as ammonia gas can be effectively trapped through electrostatic interaction with carboxyl groups, and aldehyde species can be trapped by amino groups in the film through Schiff's base formation. Suppression of aldehyde release is important for prevention of sick building syndrome. The proposed films should contribute significantly where environmental considerations are of importance. Shutava *et al.* prepared an LbL film containing tannic acid, a polyphenol of natural origin, which has ability as an antioxidant to scavenge free radicals.[299] Deposited as an outermost layer on the surface of devices, layers of polyphenol can significantly inhibit their damage by trapping free radicals before they can reach the inner layers. Their experimental results demonstrate that the polyphenol multilayers positioned as an organized protective shell on the surface of biodevices or compacted drug forms may inhibit or diminish free-radical damage of encapsulated compounds. Simple variation of the number of deposited layers changes the antioxidant properties of the assemblies. Apart from that, several research groups have reported the applications of polyelectrolyte membranes including gas separations,[300–303] pervaporation from water/organic solvent mixtures,[304–307] ion separations for nano-filtration,[308,309] and reverse osmosis membranes.[310]

The LbL films in both flat membrane form and capsule structures have been used for controlled release. Lynn and coworkers used a degradable polymer as a component of the LbL films to realize controlled DNA delivery.[311] As illustrated in Fig. 10, multi-layered films up to 100 nm thick containing a synthetic degradable cationic polymer and plasmid DNA coded with green fluorescent protein were fabricated in layer-by-layer fashion onto the surfaces of planar silicon and quartz substrates. Degradation of the former components induced release of the plasmid, which was confirmed by high levels of enhanced green fluorescent protein in the cell.

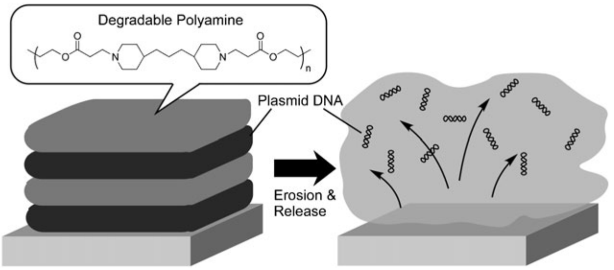

Fig. 10 DNA release from LbL film made of degradable polyamine. Reprint with permission from ref. 311, J. Zhang *et al.*, *Langmuir*, 2004, **20**, 8015. ©2004, American Chemical Society.

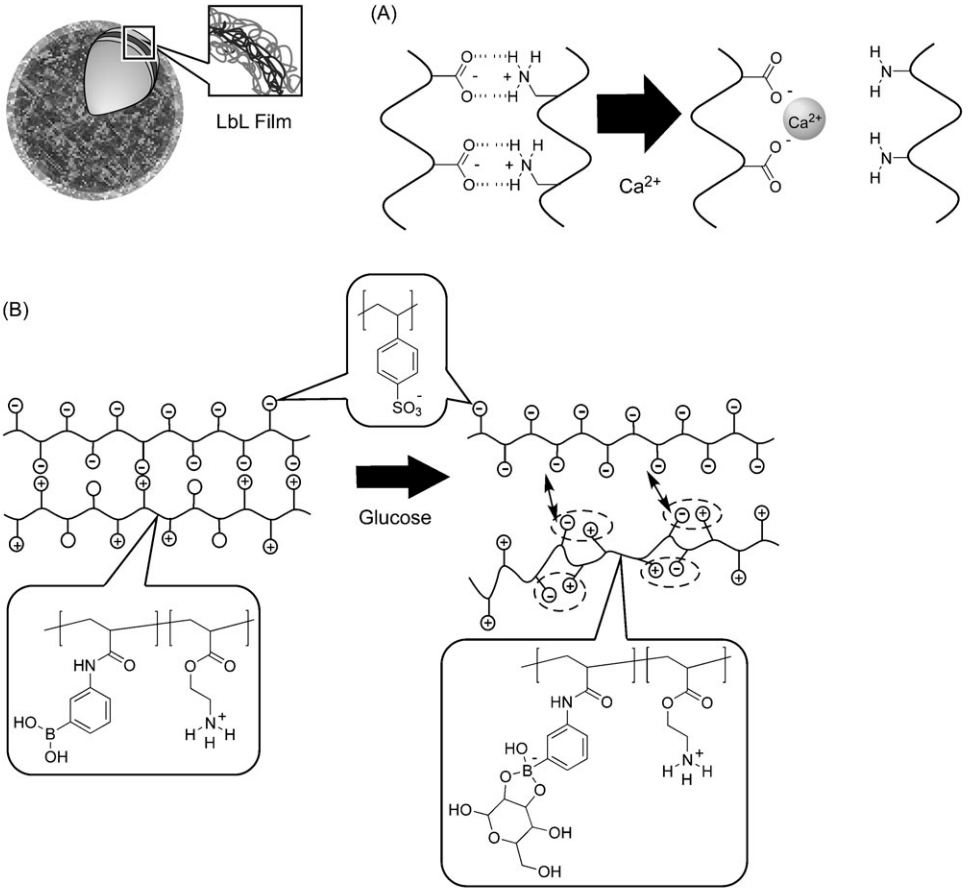

Fig. 11 Stimuli-responsive LbL capsules; (A) with stimuli of pH and Ca ion; (B) with stimulus of sugar. Reprint with permission from ref. 314, T. Mauser *et al.*, *Langmuir*, 2006, **22**, 5888. ©2006, American Chemical Society and from ref. 316, B. G. De Geest *et al.*, *Langmuir*, 2006, **22**, 5070. ©2006, American Chemical Society.

Advincula and coworkers developed pH-sensitive bipolar ion-permselective films of polyelectrolyte multilayers, prepared by LbL assembly and photocrosslinking of benzophenone-modified poly(acrylic acid) (PAA-BP) and poly(allylamine hydrochloride) (PAH-BP) with the aim of bipolar pH-switching of permselectivity for both cationic and anionic molecular probes.[312] Under basic condition, the LbL film is permeable to the cationic probe but impermeable to the anionic probe because deprotonation of free carboxylic acid at high pH promotes and suppresses permeability of cationic and anionic probes, respectively. At lower pH, the same LbL film is permeable to an anionic probe but less permeable to a cationic probe due to the protonation of free amine. Rubner, Cohen, and coworkers also reported permeability control using LbL films,[313] *i.e.*, they proposed pH-induced hysteretic gating of track-etched polycarbonate membranes that were filled with the LbL assembled polyelectrolyte multi-layers comprising PAH and PSS at high pH. Swelling/deswelling properties of the multilayers leads to gating properties of material transport through the membrane. Such stimuli responsive mechano-chemical valves can be used to gate the flow of water in microfluidic channels allowing either an open or closed state to exist at a single pH condition.

Mauser *et al.* fabricated hollow microcapsules composed of PAH and poly(methacrylic acid) (PMA) and investigated changes of the morphology and the thickness of the resulting capsules.[314] If the molecular weight of the PMA is high enough, a reversible swelling of the capsules at low or high pH can be achieved due to the enhanced entanglement of the polymers. When calcium ions were present in the solution at high pH, deprotonated carboxylic groups can complex Ca^{2+} (Fig. 11A). Only a small amount of calcium is sufficient to form a precipitate. Wang and Caruso synthesized nanoporous polymer-based spheres *via* sequential assembly of polyelectrolytes in mesoporous silica particles, followed by removal of the templates.[315] The resulting PAA/PAH nanoporous polymer spheres exhibited a high capacity for enzyme loading, with stimuli-responsive reversible loading and release of the protein triggered by changes in solution pH. The proposed systems, with nanoscale porosity and designed functionality, are envisaged to offer new opportunities for their application in biosensing, catalysis, and drug delivery. De Smedt and coworkers developed glucose-sensitive polyelectrolyte capsules through LbL assembly of cationic polymer bearing phenylboronic acid moieties and PSS.[316] Upon addition of glucose, the phenylboronic acid moieties become negatively charged and start to interfere strongly with the polyelectrolyte multilayers (Fig. 11B). An intermolecular repulsion between the sulfonate groups of the PSS and the glucose/phenylboronic acid complex is thought to be partly responsible for the disassembly of the capsules. Vancso and coworkers prepared polyelectrolyte multilayer capsules composed of polyanions and polycations of poly(ferrocenylsilane).[317] The permeability of these capsules could be sensitively tuned *via* chemical oxidation, resulting in a fast capsule expansion accompanied by a drastic permeability increase in response to a very small trigger. The redox-controlled permeability and swellability have a high application potential in materials as well as in bioscience. Lvov and coworkers developed a versatile approach for DNA encapsulation inside a biocompatible polyelectrolyte microshell, retaining the natural double-helix structure of DNA.[318] In their method, $MnCO_3$ particles as template core materials were suspended in DNA solution, and the addition of spermidine solution into stirred $MnCO_3$/DNA solution caused precipitation of a water-insoluble DNA/spermidine complex onto the $MnCO_3$ particle. The obtained mixed-component cores were covered by LbL assembly comprising biocompatible polyarginine and chondroitin sulfate. The $MnCO_3$ template particles were first dissolved, resulting in biocompatible capsules containing DNA/spermidine complex. Further decomposition of the DNA/spermidine complex led to selective release of low molecular weight spermidine to complete DNA entrapment.

The ready adaptability of LbL assembly is a great advantage in the design of chemical reactors.[319,320] Kunitake and coworkers developed the multi-enzyme reactors containing glucose oxidase (GOD) and glucoamylase (GA) prepared on an ultrafilter through which a substrate solution was passed (Fig. 12).[321] Hydrolysis of the glycoside bond in starch by GA produced glucose that was converted to gluconolactone by GOD with H_2O_2 as a co-product. Reactor ability can be optimized by adjusting the number of layers, layering sequence, and layer separation. Polyelectrolyte layers seem to be more permeable to a reaction substrate than to a condensed lipid membrane such as LB films. Bruening and coworkers immobilized gold nanoparticles within alumina porous supports through LbL assembly to form catalytic membranes (Fig. 13A).[322] These colloid-modified membranes showed remarkable conversions of 4-nitrophenol to 4-aminophenol at high flow rates in the presence of the reducing reagent, $NaBH_4$. This system reduced $>99\%$ of 0.4 mM 4-nitrophenol at linear flow rates of 0.98 cm s^{-1}. Their results indicate a turnover number >1000 mol of 4-nitrophenol per mol of gold contained within the membrane. Shchukin and Möhwald prepared PSS/PAH LbL microcapsules containing TiO_2 nanoparticles that catalyze photosynthesis of urea from inorganic precursors (CO_2 and NO_3^-) in aqueous solution (Fig. 13B).[323] In their strategy, nanosized TiO_2 was taken as a model semiconductor encapsulated inside the LbL capsules, together with poly(vinyl alcohol) (PVA) as electron donor. The TiO_2-mediated urea photosynthesis in water can be described by the equations shown in Fig. 13B. The highest yield of urea photosynthesis (37%) was achieved for

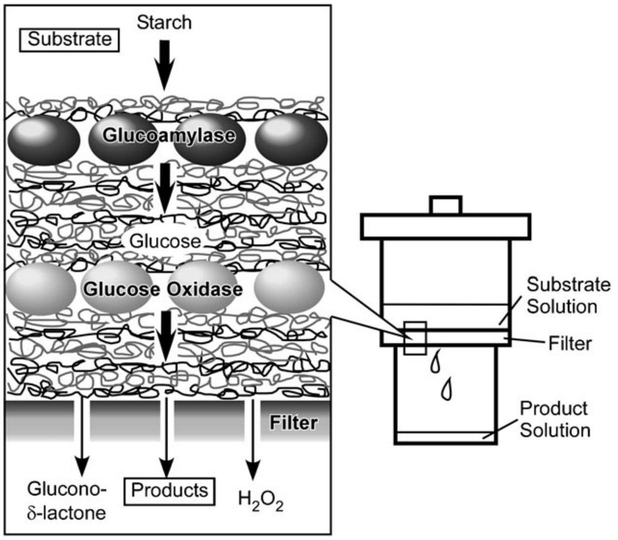

Fig. 12 Multi-enzyme reactor of LbL film on ultrafilter.

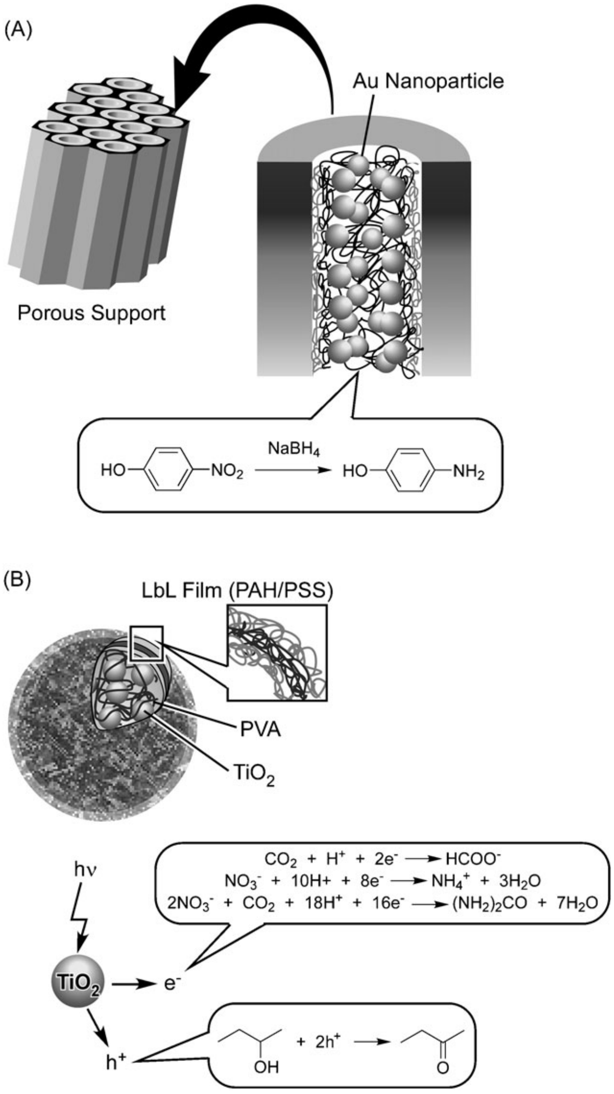

Fig. 13 LbL-type catalysts; (A) gold nanoparticle catalysts immobilized within porous support; (B) titania photocatalyst confined in LbL capsule. Reprint with permission from ref. 322, D. N. Dotzauer *et al.*, *Nano Lett.*, 2006, **6**, 2268. ©2006, American Chemical Society and from ref. 323, D. G. Shchukin and H. Möhwald., *Langmuir*, 2005, **21**, 5582. ©2005, American Chemical Society.

Cu-modified TiO_2 nanoparticles encapsulated inside the 2.2 μm PVA-PAH/PSS capsules.

LbL structures are often immobilized on the surface of a solid device such as an electrode for material sensing and conversion. For detection and digestion of paraoxon, Leblanc and co-workers prepared the LbL films with organophosphorus hydrolase (OPH).[324] In order to minimize activity loss and maintain enzyme performance, they assembled a polyelectrolyte cushion composed of five layers of positively charged chitosan and negatively charged poly(thiophene-3-acetic acid), on which OPH was adsorbed. Detecting the presence of paraoxon compounds with speed and sensitivity can be performed using the absorption and fluorescence detection methodologies. Forster, Rusling, and co-workers proposed direct electrochemical luminescence measurement for 8-oxoguanine detection, which was based on catalytic oxidation of guanine in DNA with $[Os(bpy)_2\text{-}(PVP)_{10}]^{2+}$ leading to photo-excited $Os^{II}*$ sites and subsequently electrochemical luminescence signals (PVP represents poly(vinylpyridine)).[325] Rusling and co-workers also reported a DNA damage detection system using DNA-enzyme LbL films containing myoglobin or cytochrome P450 on electrodes.[326] The DNA damage was detected by square wave voltammetry (SWV) using catalytic oxidation with $Ru(bpy)_3^{2+}$ and monitoring the binding of $Co(bpy)_3^{3+}$. In such systems electric contact between the LbL films and electrode is undoubtedly important. Calvo *et al.* reported LbL films containing glucose oxidase (GOD) and an Os-complex-derivatised PAH on an electrode.[327] The latter redox-active component can work as an electric wire to mediate electron transfer between the enzyme and the electrode. Schmidtke and coworkers integrated carbon nanotubes in GOD-containing LbL films.[328] In their approach, gold electrodes were initially functionalized with negatively charged 11-mercaptoundecanoic acid followed by alternate immersion in solutions of a positively charged redox polymer, poly[(vinylpyridine)Os(bipyridyl)$_2$Cl$^{2+/3+}$], and negatively charged GOD single-walled carbon nanotubes. Incorporation of single-walled carbon nanotubes into the LbL films did not appear to affect the redox potential of the films or the reversibility of electron transfer but did induce a 2–4-fold increase in the electrochemical response, resulting in an increase of enzymatic response to response to glucose. Such an improvement in sensor performance can be achieved easily using LbL technology because of its good versatility in film construction.

Coating with LbL films has also been used for bioprotective purposes. Krol *et al.* wrapped human pancreatic islets with polyelectrolyte LbL films.[329] While there was only a minor influence on the release of insulin, antibody recognition was significantly suppressed. Suppression of antibody recognition may be caused by exclusion of the antibody due to the small cutoff of the multilayer structure and/or masking of the corresponding epitope on the cell surface. It was suggested that the latter factor is more probable. Kotov and coworkers demonstrated antimicrobial coating using LbL assembly of silver nanoparticles.[330] Silver and silver ions are known to show effective antimicrobial activity. They prepared a nanostructured, hybrid, multifunctional composite containing clay layers implanted with starch-stabilized silver nanoparticles. The resulting composite showed excellent structural stability with no detectable levels of silver lost over a 1 month period. In addition, almost complete growth inhibition of *E. coli* over an 18 h period was observed. The amount of silver eluted from the LbL composite over a 1 month period was determined to be only 0.5–3.0 μg L^{-1}, which did not prevent growth of mammalian tissue cultures. This LbL composite was proved to show biocompatibility with a human osteoblast cell line. Not limited to these examples, LbL coating techniques have been used in several practical applications. For example, in USA and Europe, there are at least three real applications of LbL coating: (i) drug nano-encapsulation; (ii) biocompatible coating (eye lenses); and (iii) cellulose microfiber coating.[331–335]

IX. Future perspectives

In this review, various aspects of the LbL assembly, from physicochemical fundamentals to possibilities of practical applications, have been described comprehensively. Basically, the LbL method is simple, versatile, and flexible in its implementation, which permits various use based on the requirements of research projects or practical applications. Of the various features of development of LbL assembly, we would like to point out one unique aspect as a potential fruitful direction for this research area. That is the combination of the LbL technique with current-existing top-down microfabrication and nanofabrication strategies. Several pioneering examples have already appeared and are described below. Hammond and coworkers proposed the use of chemically patterned surfaces as templates for ionic multilayer assembly based on techniques using poly(dimethylsiloxane) (PDMS) stamps that had been prepared on a photolithographically prepared silicon master.[336,337] This patterning concept was realized in the preparation of photovoltaic devices consisting of TiO_2, porphyrin dyes, and polyelectrolytes. Combining the LbL technique with ink-jet printing and photolithography was demonstrated by Yang and Rubner.[338] In their method, exposure of the film to water with an appropriate pH through the ink-jet printing method lead to micro-patterning with a desirable structure. An excellent example of microfabrication of LbL films into a free-standing micro-object was performed by Lvov and coworkers who demonstrated the synthesis of an LbL self-assembled ultrathin micro-cantilever consisting of clay/polymer nanocomposites.[339] They used sequenced procedures including patterning, photo-treatment, etching, and LbL assembly (Fig. 14). Lvov and coworkers also proposed a microfluidic approach for the complex formation of polyelectrolytes and polyelectrolyte/protein microstrips on a glass surface.[340] Forry *et al.* recently demonstrated the rapid, controllable immobilization of suspended mammalian cells within microfabricated environments using combination with dielectrophoresis on a surface modified with the LbL films.[341] All these examples can be regarded as a clever fusion between top-down (microfabrication) and bottom-up approaches (LbL assembly).

Generally, limitations of the top-down approach are well appreciated, while the bottom-up approach has yet to mature. Therefore, a combination of both approaches is likely to be of importance in practical solution of nanotechnology. However,

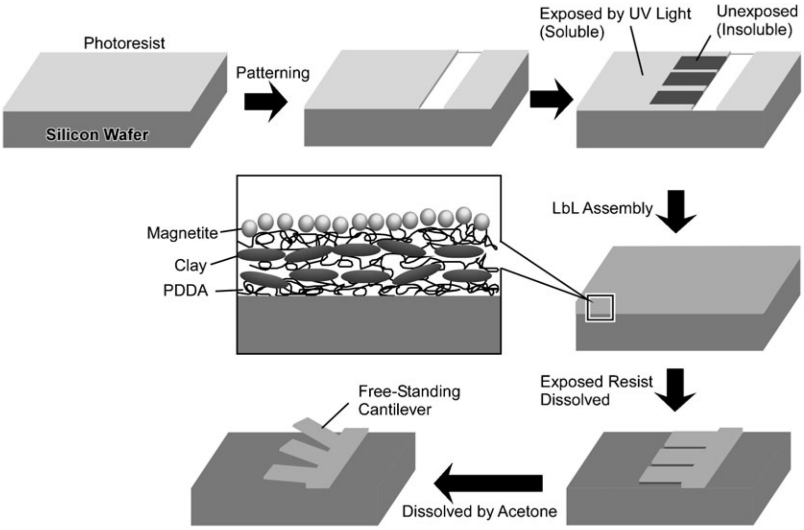

Fig. 14 Preparation of free-standing cantilever using LbL method and microfabrication techniques. Reprint with permission from ref. 339, F. Hua *et al.*, *Nano Lett.*, 2004, **4**, 823. ©2004, American Chemical Society.

currently most bottom-up research is solely of academic interest with many advanced examples such as molecular machines available, while at the same time having no practical uses. Additionally, LbL assembly methods are amenable to a wide range of adaptations because of its simple concept. Therefore, the LbL method could be the most prominent bottom-up methodology for realization of nanotechnologies originating from purely scientific ideas. Although not limited to nanotechnology, the versatility and simplicity of the LbL method is of substantial use in the advanced nanosciences where fundamental physicochemical phenomena can be examined within well-defined nanostructures, as seen in Decher's example in Fig. 8.

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