Layer-by-layer assembly: from conventional to unconventional methods

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Layer-by-layer (LbL) assembly is a powerful means for fabricating multilayer thin films with controlled architecture and composition. This feature article discusses different types of methods for LbL assembly. On the one hand, some of the conventional LbL methods are introduced, which are driven by electrostatic interactions, hydrogen bonds, step-by-step reactions, sol–gel processes, molecular recognition, charge-transfer, stepwise stereocomplex assembly, and electrochemistry. On the other hand, some of the unconventional methods for fabricating of the building blocks which can not be assembled by conventional methods are also summarized. These unconventional methods usually involve the formation of supramolecular structures *via* one type of self-assembly. These structures can subsequently be used as building blocks in another type of self-assembly. To take advantage of these conventional and unconventional methods, a great number of building blocks can be fabricated into multilayer thin films with a defined sequence structure in a designed way. It has been demonstrated that LbL methods provide new horizons for surface molecular engineering.

Introduction

The layer-by-layer (LbL) assembly is a technique of depositing multilayers. Although it has gained a rapid progress recently, the research can be traced back to the pioneering work of Iler in 1966, who reported for the first time the fabrication of multilayers by alternating deposition of positively and negatively charged colloid particles, as shown in Fig. 1.[1] As Iler pointed out, a similar technique could be applied not only to colloid particles, but polyvalent ions, surfactants, water-soluble polymers, and even proteins.

This important work did not become public until it was rediscovered by Decher and Hong.[2,3] For a clear understanding of the technique, they employed a special example for describing LbL deposition, as shown in Fig. 2. In step I, a substrate with a positively charged surface was immersed in the solution of a negatively charged amphiphile leading to the adsorption of one monolayer and to the reversal of the surface charge. Then the substrate was rinsed in pure water in order to remove the adhering solution of the negatively charged amphiphile. In step II, the substrate was dipped into a solution containing a positively charged polyelectrolyte. Again a monolayer was adsorbed but now the original positive surface charge was restored. After a second rinsing step the process could be carried out in a cyclic fashion, yielding multilayer assemblies.

The LbL technique, as schematically shown above, has shown many advantages over other methods for multilayer fabrication. (1) No complicated instruments are needed, thus it is a simple method for fabricating multilayers. The

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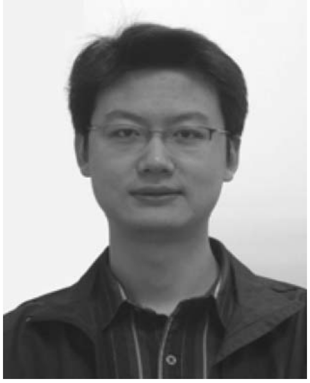

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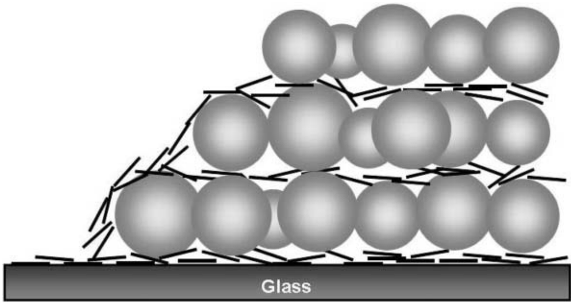


Fig. 1 Schematic cross section of a multilayer film. Spheres: colloidal silica; rods: colloidal alumina.

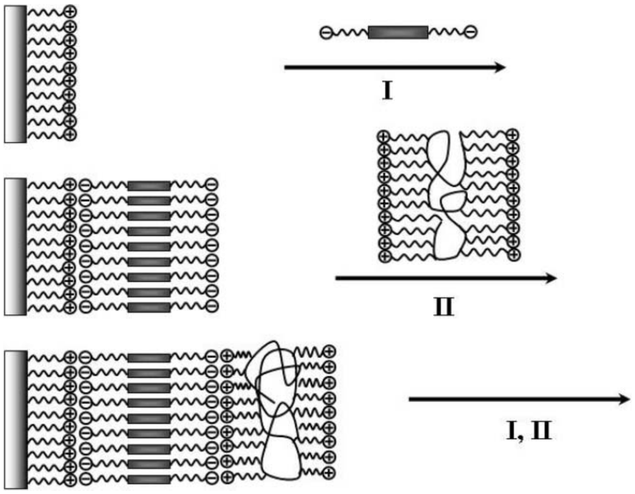
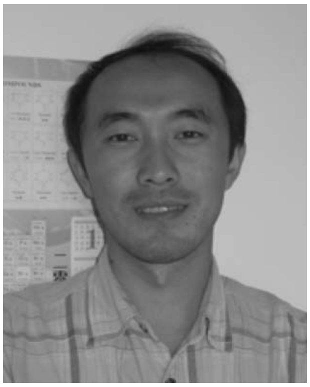


Fig. 2 The buildup of a LbL self-assembled film with anionic bipolar amphiphiles and polycations on a charged surface.

applications of this method become even more versatile, particularly after the establishment of LbL methods on the basis of different intermolecular interactions, besides electrostatic interaction. (2) It allows for incorporating various building blocks into the multilayer in a designed way. Therefore multilayer films with desirable layered supramolecular structure and integrated properties may be obtained. (3) The LbL deposition is independent of the size or shape of the substrate. It means that the LbL assembly can be realized not only on planar substrates, but also on substrates with different shapes. For example, Caruso *et al*. have demonstrated the LbL deposition on a spherical template. After dissolving the template, microcapsules were obtained.[4–8]



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In this feature article, we would like not only to review the different conventional LbL methods on the basis of different driving forces by simple alternating deposition, but also to highlight recent development of unconventional LbL methods. The unconventional methods were developed for assembling some of the building blocks, which can not be assembled by conventional methods.

Conventional LbL assembling methods

Conventional LbL methods refer to LbL methods that are driven by different driving forces. They allow for the fabrication of a large variety of building blocks into multilayer thin films without prior or post treatment. Different LbL methods are suitable for different building blocks. They have their advantages as well as disadvantages. In some cases, the advantages and disadvantages are convertible. In contrast with the unconventional LbL methods discussed later that involve a two-step assembling process, conventional LbL methods include simply alternating deposition of building blocks with complementary interactions or structures.

1 Electrostatic interaction

The electrostatic interaction is the main driving force for LbL assembly, which in this case that requires the building blocks are water-soluble and multi-charged species, such as polyelectrolytes, proteins and enzymes, colloid particles, and oligo-charged organic compounds.[9–12] Provided that the process of the multilayer formation is simply based on electrostatic attraction, it does not require an exact positional matching of the charged groups. Therefore we are able to incorporate more than one building block into the multilayer, and if necessary, different building blocks are incorporated in a designed layer sequence. The electrostatic LbL assembly is performed in aqueous solution; thus it is convenient to fabricate LbL multilayers in an automated way by using a LbL deposition machine. It should be noted that there is no clear interface structure for the polyelectrolyte multilayer. In many experiments on multilayer films composed of flexible and strong polyanions and polycations with one charged group per monomer unit, X-ray reflectograms have exhibited only so-called Kiessig fringes that arise from the interference of X-ray beams reflected at the substrate-film and the film-air interface, respectively. In other words, the adjacent layers are interdigitated to some extent in polyelectrolyte multilayers.

2 Hydrogen-bonded LbL assembly

Hydrogen-bonded LbL assembly was first demonstrated by Stockton and Rubner[13] and Zhang and co-workers[14] simultaneously in 1997. Polymers with hydrogen bond donors and acceptors can be employed as building blocks for fabricating LbL films in this way. For example, as shown in Fig. 3, multilayer thin films can be fabricated by alternating

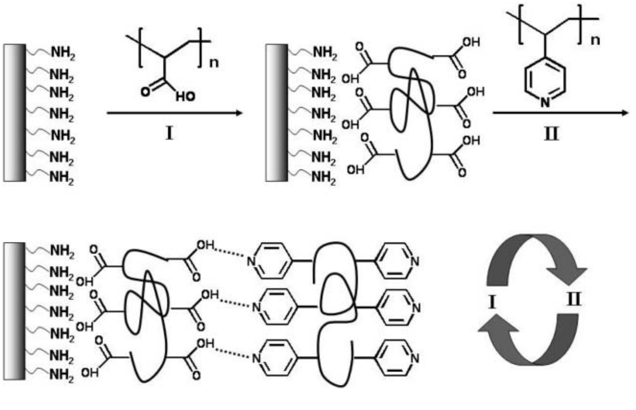

Fig. 3 Fabrication of LbL self-assembled multilayer film *via* hydrogen bonding between carboxylic acid groups and pyridine groups.

deposition of poly(acrylic acid) (PAA, hydrogen bond donor) and poly(4-vinylpyridine) (PVP, hydrogen bond acceptor) in organic solvent on the basis of hydrogen bond formation, which is identified by FT-IR spectroscopy. Although PAA can self-aggregate with itself, it prefers to form coaggregates with PVP through intermolecular hydrogen bonds when alternating deposition is carried out. Another example is the multilayer of polyaniline in alternating deposition with poly(vinylpyrrolidone), or poly(vinyl alcohol), or poly(acrylamide), or poly(ethylene oxide). In the latter systems, the building blocks are not able to form hydrogen bonding with themselves, hence the complementary hydrogen bonding between donors and acceptors can make the process feasible.

Hydrogen bonds are sensitive to their environment. Once formed, hydrogen bonds can be destroyed by changing the environment. Taking the advantage of this feature of hydrogen bonds, Sukhishvili and Granick have demonstrated that LbL multilayers of poly(methacrylic acid) and poly(vinylpyrrolidone) can be stable up to pH 6.9, but dissolve when the pH is raised above this point. Therefore, hydrogen-bonded LbL assembly can be used to fabricate layered, erasable, ultrathin polymer films.[15,16] We have also studied systematically the effect of solvents on hydrogen-bonded multilayer films.[17] One of the interesting findings is the structure variation of PAA/PVP LbL film after immersing in a basic aqueous solution.[18–21] At the very beginning of the immersion, PAA from the multilayer film dissolves into the basic solution because of the destruction of hydrogen bonds; and then the remaining PVP undergoes a gradual reconformation, producing microporous films. The microporous films exhibit different pore size and distribution depending on the chemical structure of building blocks, pH value and temperature of the solution, time of immersion, nature of substrate *etc*. For example, after immersion in pH = 13 NaOH aqueous solutions at 25 °C for different periods of time, the AFM images feature a series of microporous films with different surface coverage, depth, and shape of the holes. It was shown that the spinodal holes, several hundred nanometers in diameter, grow with time. During immersion from 10 to 180 min, the coverage increases from 10 to 30% and depth of the holes from approximately 12 to 35 nm, respectively.

3 Step-by-step reaction for LbL assembly

Step-by-step reactions provide an alternative for fabricating robust multilayer films, as introduced initially by Mallouk and co-workers.[22] They have demonstrated metal-phosphate/phosphonate chemistry for a multilayer synthesis based on sequential adsorption of components of zirconium 1,10-decanebisphosphonate, $Zr(O_3PC_{10}H_{20}PO_3)$. As shown in Fig. 4, in the first step, the Si substrate was exposed to a warm aqueous solution of a silanol, producing a monolayer of covalently anchored phosphonate groups. After washing with water, the surface was exposed at ambient temperature to aqueous $ZrOCl_2$ solution, washed, and then exposed to aqueous 1,10-decanebisphosphonic acid. Repetition of the second and third steps led to a multilayer film on the basis of coordination bonds. The success of this method derives from the thermodynamic stability of this layered solid, which crystallizes spontaneously when the two soluble components are mixed.

What types of chemical reactions are suitable for multilayer fabrication? So far many types of chemical reactions have been used for LbL deposition, and usually such chemical reactions have the following common features, including mild reaction conditions, good control, and high yield *etc*. Examples include oxidative formation of sulfur–sulfur bonds,[23] diisocyanate and diamine polymerization, isocyanate/hydrolysis polymerization,[24] and aminooxy/aldehyde Heck reaction,[25] acyl chloride/hydroxy interactions[26,27] *etc*. We took the advantage of the coordination bonds between Cu^{2+} and pyridine groups to construct LbL multilayers of poly(4-styrenesulfonate) (PSS) $PSS(Cu)_{1/2}$/PVP, and then prepared a PSS-Cu_2S nanoparticle/PVP hybrid film by diffusing H_2S gas into the multilayer film so that it could react with Cu^{2+}.[28] Very recently, as shown in Fig. 5, Caruso and co-workers reported the LbL assembly multilayer films using click chemistry between of PAA with azide and alkyne functionality.[29] Because click reactions can be performed under extremely mild conditions and with high yield, this chemistry is anticipated to become widely used for constructing polymer thin films, particularly for systems that can not be fabricated using traditional LbL assembly, such as non-charged, non-H-bonding polymers.

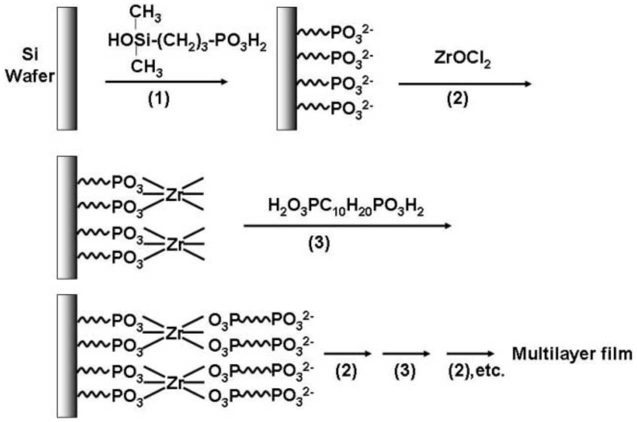

Fig. 4 Sequence of adsorption steps for self-assembly of divalent metal phosphonate films on the basis of coordination bonds.

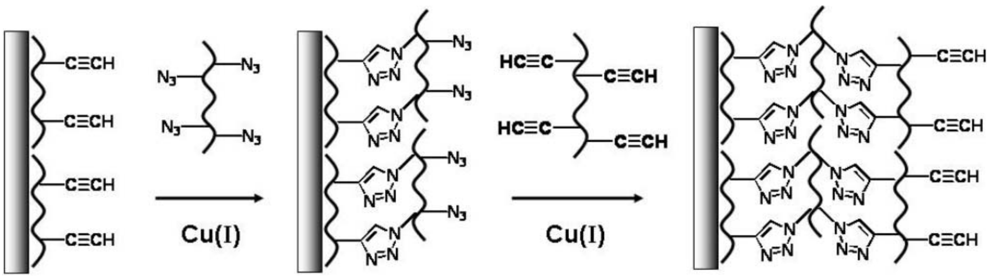

Fig. 5 LbL assembly of polymer films using click chemistry.

4 Metal oxide gel films from a surface sol–gel process

A surface sol–gel process has been introduced by Kunitake and co-workers for the preparation of nanocomposite thin films by means of stepwise adsorption of alkoxides,[30] as shown in Fig. 6. The fabrication process is composed of four steps: chemisorption of alkoxides, rinsing, hydrolysis of the chemisorbed alkoxides, and drying. Those authors have demonstrated that the surface sol–gel process is applicable to various alkoxides of titanium, zirconium, silicon, indium, tin and vanadium.[31] In addition, this method has been employed to incorporate organic dyes, amino acids and sugar compounds into such gel films to conduct molecular imprinting.[32] Recently, by use of this surface sol–gel process, some ultrathin nanocomposite coatings with new functions were produced, such as biocompatible surfaces,[33] antibacterial coatings,[34] and nonlinear optical films.[35]

5 Molecular recognition and bio-recognition

Molecular recognition is a specific interaction between host and guest systems, which provides another driving force for LbL assembly. Ringsdorf and co-workers[36] have extensively studied the layered architecture of streptavidin and biotin-labeled biomolecules. A sophisticated example is the preparation of a supramolecular triple layer, streptavidin/concanavalin A/streptavidin, as shown in Fig. 7, by connecting these components through a biotin-sugar linker. Hong *et al.*[37,38] have extended the concept of bio-recognition at the air/water interface to LbL deposition the solid/liquid interface and assembled multilayers of streptavidin and biotinylated polylysine. Almost simultaneously, Bourdillon *et al.*[39] have employed antibody/antigen interactions for constructing glucose oxidase multilayers on the surface of a glassy carbon electrode, as a step toward developing high-performance biosensors. Along the same line of research, different type of biospecific interactions between sugar and lectin,[40,41] or avidin and biotin[42] can be directly applicable to the alternate assembly of elaborate protein architecture.

Beyond bio-recognition, specific interactions between host and guest systems can also lead to LbL assemblies.[43] A β-cyclodextrin dimer is found to be effective in preparing a LbL multilayer of positively charged ferrocene-appended poly(allylamine) on the basis of strong β-cyclodextrin–ferrocene host–guest interaction. In order to enhance the host–guest interaction, Reinhoudt and co-workers have used multivalent supramolecular interactions for the LbL assembly.[44] They have shown that adamantyl-terminated dendrimers (generation 5; 64 adamantyl end groups) bind to cyclodextrin self-assembled monolayers on gold surfaces, leaving multiple guest groups exposed to the solution available for complexation of hosts from solution. The alternating deposition of cyclodextrin modified gold nanoparticles and adamantyl-terminated

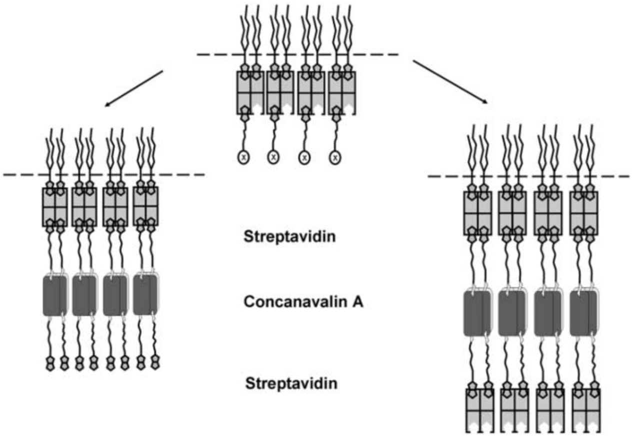

Fig. 7 LbL self-assembly of streptavidin and concanavalin A through bio-recognition at the air/water interface.

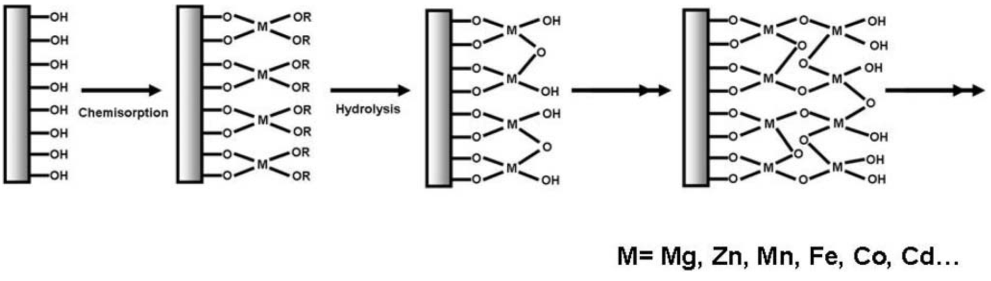

Fig. 6 Schematic illustrations of three types of LbL adsorption based on the surface sol–gel process.

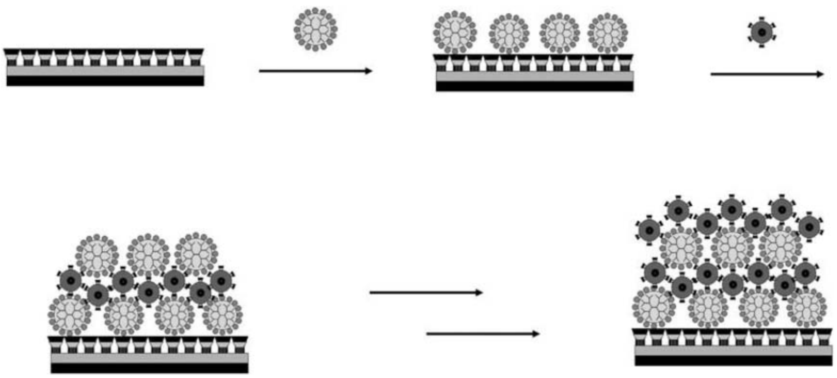

Fig. 8 LbL assembly scheme for the alternating adsorption of adamantyl-terminated dendrimer and cyclodextrin modified Au nanoparticles onto cyclodextrin monolayers.

dendrimers, as shown in Fig. 8, provides a supramolecular approach for the stepwise construction of multilayer thin films. This approach constitutes a general nanofabrication paradigm for the integration of organic, inorganic, metallic and biomolecular components while retaining the interfacing supramolecular specificity.

6 Charge-transfer interaction

Yamamoto and co-workers[45] have introduced a way for building up multilayered films by consecutive adsorption of two types of nonionic polymers, which have electron-accepting groups (*e.g.* 3,5-dinitrobenzoyl group) and electron-donating groups (*e.g.* carbazolyl group), respectively, at the ends of the side chains. The formation of such multilayered films is based on the charge-transfer (CT) interactions between donor polymer and acceptor polymers. Thus, the films obtained have periodic layers of CT complexes as shown in Fig. 9. Moreover, the films can be prepared in organic solvents, which makes it possible to homogeneously introduce hydrophobic functional groups into the LbL films.[46–50] The application of such films as conductive or nonlinear optical materials is greatly anticipated.

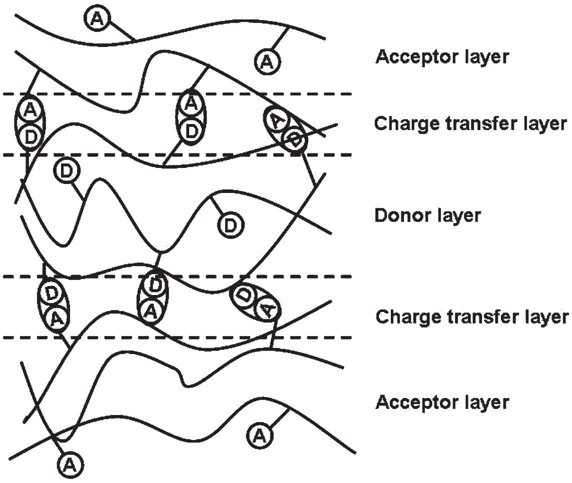

Fig. 9 Side-view illustration of the deposited film. For simplicity the carbazolyl groups and 3,5-dinitrobenzoyl groups are represented as D and A, respectively. Pairs of D and A forming charge-transfer complexes are circled.

7 Stepwise stereocomplex assembly

Stereocomplexes are formed between sterically well-defined synthetic polymers in certain solvents. Although stereocomplex formation between stereoregular polymers is well documented, Akashi and co-workers were the first to utilize the characteristics of the stereocomplex for LbL deposition of ultrathin polymer assemblies on the substrates.[51–53] For example, as shown in Fig. 10, isotactic (it-) and syndiotactic (st-) poly(methyl methacrylate)s (PMMAs) can form stereocomplexes of a double stranded helical structure in solution, in which each it-PMMA is surrounded by two chains of st-PMMA. For a stepwise stereocomplex of stereoregular PMMAs at the liquid/solid interface, it was shown that a similar phenomenon as in solution occurred. In other words, the stepwise stereocomplex assembly occurs during the step from physically adsorbed it-PMMA to st-PMMA, and includes a molecular rearrangement that is initiated by the penetration of st-PMMA into it-PMMA layer. The building blocks that can be fabricated in this way are limited, and the assembly is affected by conditions such as solvent species, PMMA concentration and PMMA molecular weight.

8 Electrochemical LbL deposition

Electrochemical LbL deposition refers to a potentiodynamic method for LbL assemblies as introduced by Cheng and Dong.[54] As an example, a gold electrode was modified by a self-assembled monolayer (SAM) of cysteamine, denoted as Au/Cyst SAM. For electrochemical growth, Au/Cyst SAM was alternatively placed in a solution of Keggin-type

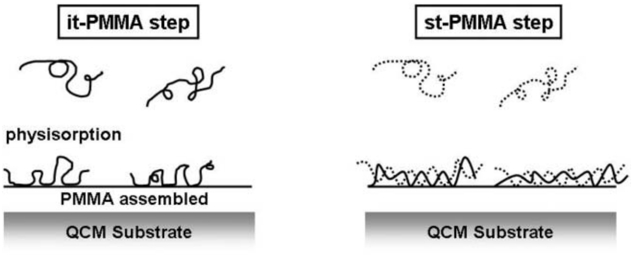

Fig. 10 Schematic representation of the physical adsorption of it-PMMA onto st-PMMA, including a molecular rearrangement that was initialized by the penetration of st-PMMA into it-PMMA layers.

$SiMo_{11}VO_{40}^{5-}$ and quaternized PVP partially complexed with osmium bis(2,2′-bipyridine) chloride; cyclic potential sweeps were simultaneously conducted at a scan rate of 100 mV s^{-1} for 25 cycles in a potential range between 0.65 and -0.15 V where the redox reactions of $SiMo_{11}VO_{40}^{5-}$ took place in solution. This method has been proven to be an effective method for multilayer assembly of electroactive species for the fabrication of electrochemical sensors.[55,56] In contrast with the normal LbL method, the electrochemical LbL deposition works well with salt-containing solutions without the drawback of competitive adsorption from the salt ions, thus producing uniform films. Moreover, between each modification, the resulting electrode is washed only with water, without any need for the drying steps that are commonly required and used in the normal LbL method.

In an attempt to control the lateral growth and termination in a patterned surface, Gao, Sun *et al.* used electrophoretic deposition to realize spatially selective deposition of multilayer films.[56,57] Taking LbL deposition of positively charged poly(diallyldimethylammonium chloride) (PDDA) and negatively charged CdTe nanocrystals on Au substrates as a example, it was demonstrated that the depositions of PDDA and CdTe could be facilitated by maintaining the polarity of the electrode opposite to the sign of the charge of the deposited material (favorable deposition). In contrast, the deposition can also be prohibited when the polarity of the electrode is always the same as the sign of the charge of the deposited material (unfavorable deposition). A similar concept could be applicable to the construction of a thickness- and area-controlled biopatterns composed of multi-enzymes as well as multiple biomaterials.[58]

Unconventional LbL methods

Although the above mentioned LbL methods, which are based on the basis of different driving forces have been well used for multilayer fabrication of many types of building blocks, there are still many other building blocks which can not be fabricated by such conventional methods. For example, the conventional LbL methods are not feasible for fabricating multilayers with building blocks of single charged, electrically neutral, or water-insoluble species. However, there is an increasing need to assemble these species for different functional assemblies. The following unconventional LbL methods are being developed for this purpose. The key idea of these approaches includes more than one step in the assembly process. One possibility is that supramolecular structures formed *via* one type of self-assembly can be subsequently used as building blocks in LbL assembly. The other possibility is to undertake some types of post-treatment after LbL assembly. It is anticipated that such unconventional LbL methods provide potentially useful routes to supramolecular architectures that have higher levels of structural complexity, more compositional combinations, and/or more functionalities.

1 Inclusion complexes

Inclusion complexes are a type of supramolecular approach that renders the uncharged species charged and water-insoluble species water-soluble. After such a supramolecular modification, some of the species may become organizable and then may be fabricated into multilayer thin films in a designed sequence. One of the successful examples is given by Ikeda *et al.*[59] As shown in Fig. 11, the first type of self-assembly was to employ cationic homooxacalix[3]arene to form an inclusion complex with fullerene. In this way the water-insoluble fullerene becomes not only water-soluble, but also positively charged. The second type of self-assembly was the LbL alternating deposition of the inclusion complex and an anionic porphyrin polymer for fabrication of multilayer thin films. The as-prepared multilayer film demonstrates efficient photocurrent generation with a quantum yield as high as 21%. It seems that this noncovalently linked system features photocurrent flow from the porphyrin units *via* the fullerene units to the electrode as in the case of covalently linked dyad or triad systems, but it can overcome synthetic difficulty in covalently linking all of the thin-layer-forming units, donor unit, and acceptor units in one molecular system.

One more example of supramolecular multilayers with high levels of compositional and structural complexities was demonstrated as follows. It involves the formation of stable host–guest complexes of bolaamphiphiles and cyclodextrins, followed by sequential LbL deposition of multilayered films by these complexes in combination with anionic polystyrene sulfonate polymer chains.[60]

2 Noncovalent modification

Noncovalent modification is another choice to render inorganizable species organizable. Noy and co-workers employed noncovalent modification to attach 1-pyrenepropylamine hydrochloride onto the surface of carbon nanotubes.[61] The modification was based on the combined interaction of the hydrophobic effect and electrodonor/acceptor interactions. The carbon nanotube modified in this way became positively charged, which could be exploited in LbL deposition of polyelectrolytes as shown in Fig. 12. Unlike covalent

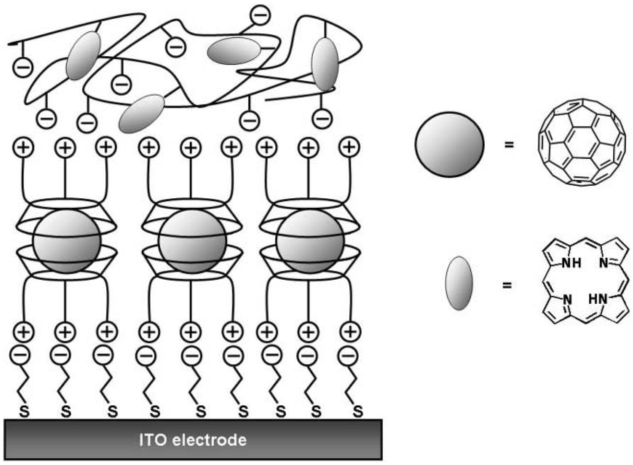

Fig. 11 Schematic representation of LbL self-assembly with inclusion complexes as building blocks.

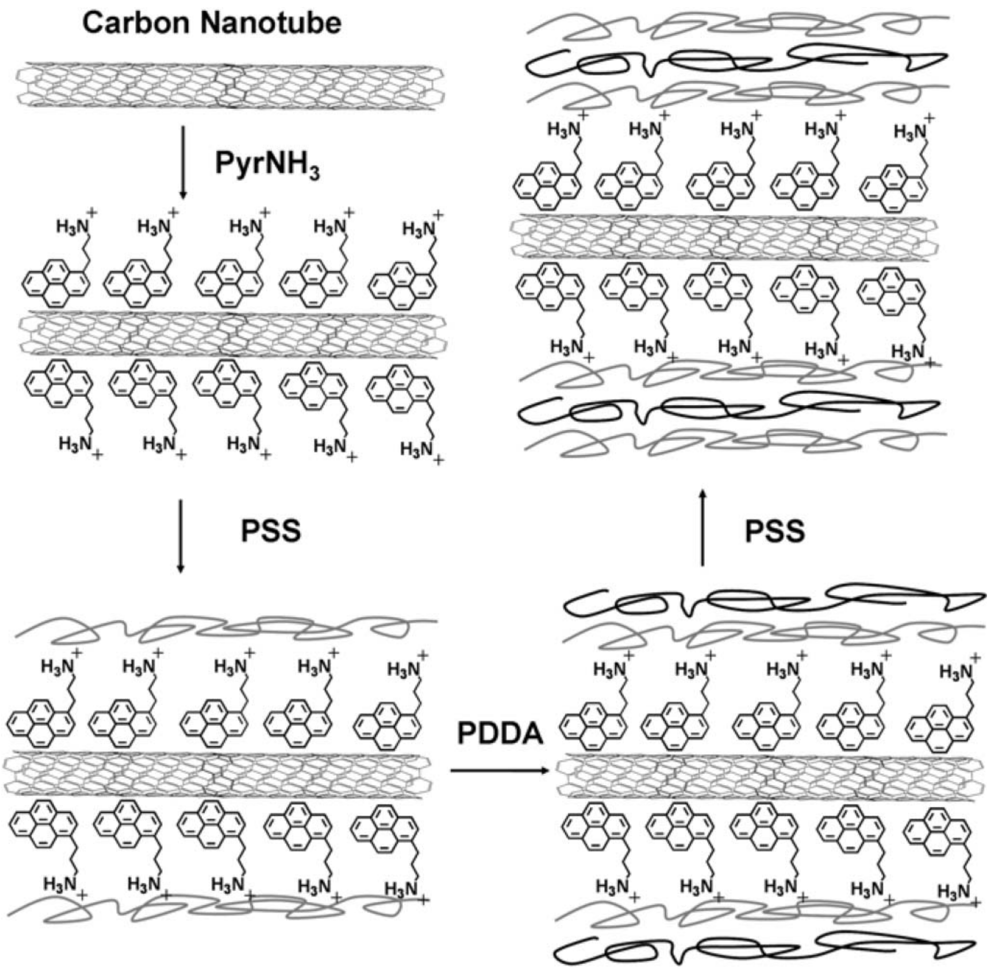

Fig. 12 Schematic representation of LbL self-assembly with carbon nanotubes as building blocks. The carbon nanotubes are modified noncovalently by charged pyrene molecules.

modification, noncovalent modification to the nanotube core typically preserves the sp^2 hybridization of the carbon atoms and, consequently, the unique electronic properties of the nanotube.

To unlock the technological potential of carbon nanotubes in devices and sensors, the carbon nanotubes need to interface with a variety of other materials ranging from inorganic materials to organic and polymer coatings to biomolecules. Methylene blue (MB), a polynuclear aromatic electroactive dye, was introduced in a noncovalent coating on the single-walled carbon nanotubes (SWNT), forming a new type of electrochemically functional adsorptive MB–SWNT nanostructure.[62,63] Furthermore, the adsorption of MB onto the nanotubes was found to solubilize the formed MB–SWNT nanostructure into water and to facilitate the LbL assembly of the prepared electrochemically functional nanostructure into a nanocomposite. In fact, the noncovalent modification can also be used to modify SWNT to be positively charged and negatively charged, respectively. Then homogeneous SWNT/SWNT multilayers can be fabricated without the introduction of inert polyelectrolytes. It is believed that such noncovalent modification combined with LbL deposition may find numerous applications in the development of electronic nanodevices, such as biosensors and photovoltaic cells for practical applications.

3 Coordination polyelectrolyte

Another precursor method was introduced by Kurth and coworkers that involved a two-step self-assembly process: first, metal ions were reacted with polytopic ligands to form a charged metallosupramolecular coordination polyelectrolyte, subsequently alternating adsorption with negatively charged polyelectrolytes generated molecular films.[64,65] The synthesis of coordination polyelectrolytes is shown in Fig. 13. Reaction of 1,4-bis(2,2′:6′,2″-terpyrid-4′-yl)benzene with metal ions in a 1 : 1 ratio in solution gave the coordination polyelectrolytes, which were referred to as metallosupramolecular coordination polyelectrolytes because of the overall positive charge. Their high positive charge allowed for assembling these units on interfaces through electrostatic LbL deposition. This unconventional method for LbL assembly opens a novel route for the integration of functional supramolecular units in ultrathin multilayers. The combination of molecular recognition by coordination of metal ions and electrostatic interactions may permit assembly of a wide variety of multilayered structures with intriguing properties.

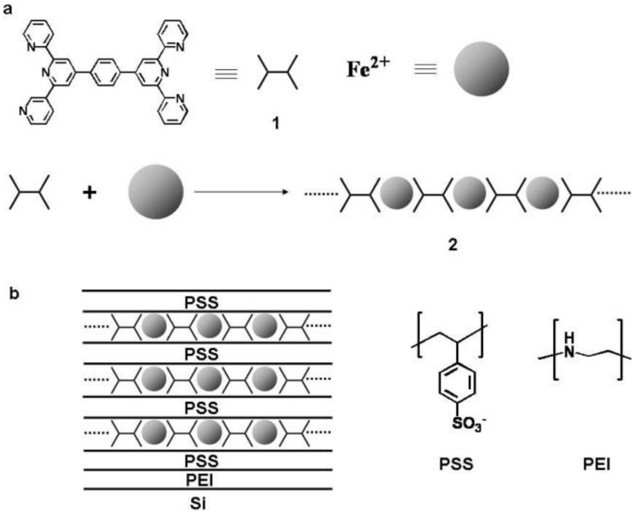

Fig. 13 (a) Ligand **1** and metal ions in a 1 : 1 ratio form the coordination polyelectrolyte **2**. The counterions are omitted for clarity. (b) Assembly of multilayers by sequential deposition of oppositely charged polyelectrolytes. PEI = polyethyleneimine, PSS = poly(styrene sulfonate).

4 Electrostatic complex formation

An electrostatic complex for the fabrication of LbL films can be described as follows:[66] first, polyelectrolytes were mixed with counter-charged molecules in aqueous solution to form electrostatic complexes; second, the complexes were deposited alternatively with counter-polyelectrolytes to form LbL films. Electrostatic complex formation is a convenient way to fabricate LbL self-assembled multilayer films with embedded charged organic molecules.[67–69] Although this method has been used to introduce charged molecules into LbL films,[70] it is not so easy to introduce singly charged molecules into LbL films in a controlled way and with high loading capacity. We have demonstrated how to introduce single charged molecules into LbL films with high loading and in a controllable manner by combining macromolecular complex formation in solution and LbL assembly at the solid/liquid interface.[71] Taking an example, as shown in Fig. 14, sodium 9-anthracenepropionate (SANP) as a negatively charged moiety was used to form a complex with positively charged PDDA, PDDA–SANP in short, and multilayer films were fabricated by alternating deposition of the PDDA–SANP complex with PSS at the solid/liquid interface. It is well known that small molecules, such as SANP, can diffuse into LbL films of PDDA/PSS. However, the amount of SANP assembled in this method was much larger than that the diffusion method, and moreover a controllable amount of SANP could be incorporated by adjusting the initial concentration of SANP in the PDDA–SANP complex solution. In addition, we have found, interestingly, that the SANP can undergo a photoreaction in the LbL films with a quantum yield four times higher than that in bulk solution, thus suggesting that LbL films could be useful as nanoreactors.

It should be noted that the combination of macromolecular complexes and LbL deposition allows not only for incorporation of single charged moieties into LbL films, but also for controlled release of them from LbL films. For example, when immersing a LbL film of PDDA–SANP/PSS into an aqueous solution of Na_2SO_4, the SANP could be released from the film quickly depending on the ionic strength of the solution. An interesting finding is that after releasing SANP, the LbL film has been endowed the property of charge selectivity. That is to say, the as-prepared LbL film can readsorb only negatively charged moieties, whereas it repels positively charged moieties. As to a PDDA/PSS film fabricated by conventional method, it adsorbed negatively charged SANP and positively charged (anthracen-9-ylmethyl)trimethylammonium bromide (ATAB) with comparable amounts, and no charge selectivity was observed. However, the loading capacity of SANP in a PDDA–SANP/PSS film with "imprinting sites" was seven times higher than that in a PDDA/PSS film, but ATAB hardly

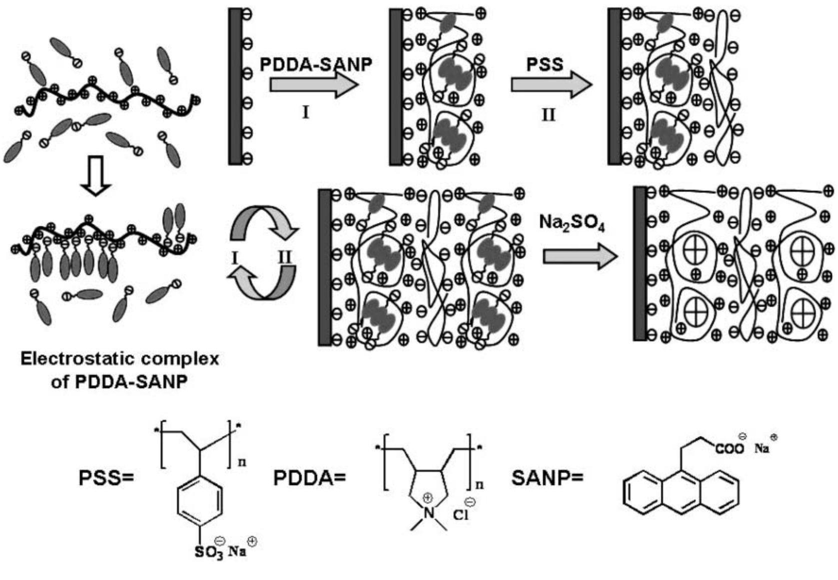

Fig. 14 Schematic illustration of LbL assembly by electrostatic complex formation: step 1, SANP tethered to PDDA in solution; step 2, LbL self-assembly of PDDA–SANP/PSS. LbL film with charge selectivity can be obtained by removing SANP from the film.

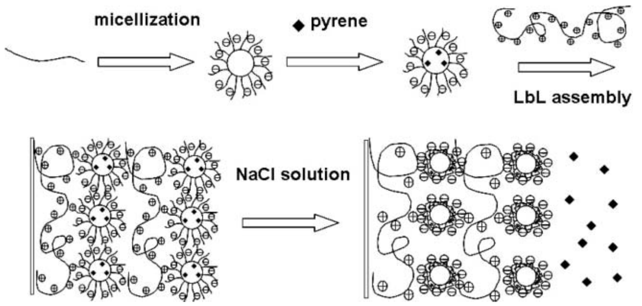

Fig. 15 Schematic representation of the incorporation of pyrene into micelles, LbL deposition of micelles and PDDA, and release of pyrene from the multilayer film.

adsorbed in PDDA–SANP/PSS film. It is believed that such a concept can be applicable to other singly charged moieties, such as positively charged moieties. In that case, after releasing the positively charged moieties the resulting LbL film could readsorb positively charged moieties and repel negatively charged moieties. Therefore, this line of research provides a new approach for fabricating thin film with selective permeability, leading to establishing probably LbL surface imprinting.

5 Block copolymer micelles

Amphiphilic block copolymers are able to self-organize into core–shell micellar structures in selective solvent. Small water-insoluble molecules can enter the cores of such micelles spontaneously and can be released from the micelles under special conditions. Although Kataoka and co-workers introduced core–shell structured hydrogel thin films on surfaces by alternating deposition of poly(ethylene glycol)-*b*-poly(D,L-lactide) micelles and poly(allylamine), this method had limited applications because it involved complicated procedures. These included stabilization of the micelles by core polymerization and shell hydrolysis to make the surface of micelles bear reactive aldehyde groups, and finally cross-linking between the micelles and poly(allylamine) to form a Schiff base between the layers.[72,73] In order to take advantage of hydrophobic cores of the block copolymer micelles, we incorporated water-insoluble molecules, *e.g.* pyrene, into the hydrophobic micellar cores of poly(styrene-*b*-acrylic acid) and then employed the loaded block copolymer micelles as building blocks for LbL assembly.[74] As shown in Fig. 15, the block copolymer micelles of poly(styrene-*b*-acrylic acid) with acrylic acid on the shell functioned as polyanions, allowing for LbL assembly by alternating deposition with polycations. Similarly, there is linear growth for the multilayer fabrication except for the first three bilayers.

The same concept can be extended to incorporate different water-insoluble molecules, such as azobenzene, for LbL assembly.[75] It is well known that azobenzene can undergo a reversible photoisomerization under UV irradiation, but the rate of photoisomerization is faster in solution than in solid films. For a multilayer films of azobenzene loaded poly(styrene-*b*-acrylic acid) micelles and PDDA, we have found, interestingly, that the photoisomerization of the azobenzene in the multilayer film was several minutes, which was much faster than for normal solid films, but similar to that in dilute solutions, suggesting a way for enhancing the photophysical properties in the LbL films. Very recently, it was also demonstrated that positively and negatively charged block copolymer micelles can be used to fabricate micelle/micelle multilayer films.[76,77] The films prepared could show tunable optical properties, with strong antireflective property, with light transmission above 90%.

6 Methods for fabricating robust LbL multilayers

Electrostatic interaction is a main driving force within the neighboring layers of polyelectrolyte multilayers. Normally, multilayered films based on electrostatic interaction tend to be affected by the environmental conditions, *e.g.* pH values of solutions, nature of solvents, ionic strength in solutions, *etc*. So how to enhance the stability of ionic self-assembled multilayers is a problem we need to address. In order to solve this problem, we have proposed a method by combining the LbL deposition and post-photochemical reaction.[78] First, a diazoresin (DAR), which is a reactive and water-soluble positively charged polyelectrolyte, was employed as one of the building blocks for alternating deposition with PSS, leading to the formation of multilayer assemblies of DAR/PSS. Secondly, upon UV irradiation, DAR was converted into its phenyl cationic form after releasing nitrogen and then a S_N1 type of nuclear displacement by sulfonate occurred, as shown in Fig. 16. In this way, the ionic interaction in between the layers was converted into covalent bonds, therefore the stability of the multilayer thin film was significantly improved.

The advantage of the above method for fabricating stable multilayer thin film can be demonstrated as follows. It allows for construction of robust multilayers from aqueous solution *via* electrostatic interaction, or organic solution *via* hydrogen bonding. Stable multilayer thin film can be easily prepared simply by post-UV irradiation. Up to now, we have found that the concept to form covalently attached multilayer films is not

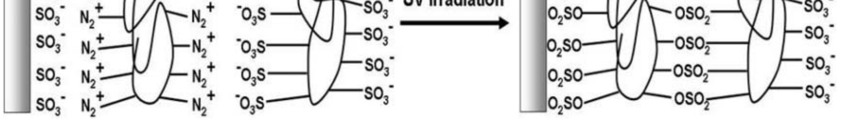

Fig. 16 Schematic representation for structural changes of multilayer assemblies which were initially based on electrostatic interactions. Upon UV irradiation the polymer chains were covalently crosslinked.

limited to the reaction of DAR with sulfonate bearing building blocks such as PSS, but also works with building blocks bearing –COOH, $–PO_3^{2-}$ or –OH groups.[79,80] This method may find application in the fabrication of stable sensor devices, patterned surface structures and ultrathin films for corrosion-resistant coatings. For example, covalently attached multilayer films of DAR and porphyrin and phthalocyanine formed on electrode surfaces can significantly improve the lifetime of resulting sensors of chemically modified electrodes. Nanoparticles modified with sulfonate or carboxylic groups can be exploited in a similar two-step treatment for forming very stable nanocomposite coating.[81]

It should be noted that post-thermal induced chemical reaction was introduced by Bruening and co-workers to construct stable LbL films. They used poly(allylamine hydrochloride) (PAH) and PAA to fabricate multilayer films, and the subsequent heat treatment induced the formation of amide bonds, through which the films were crosslinked and their stability was thus greatly improved.[82] Moreover, the post-chemical reaction in between the LbL layers can be also used for fabricating functional thin films. As an example, pyrolysis of the PDDA/poly(amic acid) LbL films by heating to 1000 °C proceeded *via* the formation of subsequent carbonization of a polyimide intermediate which ultimately produced a graphite-like carbonaceous film with conductivities in the 150–200 S cm^{-1} range.[83]

Outlook

In summary, we have reviewed different LbL methods which allow for the fabrication of a great variety of building blocks in controlled architectures and compositions. Such a line of research provides numerous ways for fabricating functional surfaces, leading to new horizons of surface molecular engineering. No matter whether the conventional or the unconventional LbL method is employed, each method has its own scope of applications as well as limitations. The combination of different methods may facilitate the assembly of thin film materials with complex and elaborate structures for the integration of functionalities.

The LbL research is not limited to the laboratory, but it has been extended from laboratory to practical applications. In view of practical application, the LbL method is simple but not so efficient. For example, it takes about 20 min to reach equilibrium adsorption in every step, so several hours are need to build up a multilayer of hundreds of nanometers in thickness. In order to develop a more efficient assembly technique, a new approach of spin-assisted LbL assembly (SA-LbL) has been suggested that combines both spin coating and LbL techniques.[84–86] Although SA-LbL is not feasible for all types of building blocks, it provides a cost- and time-efficient technology for the fabrication of multilayered films on planar substrates.

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