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Unconventional Layer-by-Layer Assembly for Functional Organic Thin Films

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1. Introduction

The layer-by-layer (LbL) assembly is a powerful technique for fabricating multilayer thin films with controlled architecture and functions (Zhang & Shen, 1999; Decher & Schlenoff, 2002; Hammond, 2004). Although the research could be traced back to pioneering work of Iler in 1966 (Iler, 1966), this important work did not become public until it was rediscovered by Decher and Hong in the beginning of 1990s (Decher & Hong, 1991a, 1991b; Decher et al., 1992). Since then, the field of LbL has gained rapid progress. Besides electrostatic driven LbL assembly (Decher, 1997), many different intermolecular interactions, such as hydrogen bonding (Wang et al., 1997; Stockton & Rubner, 1997), charge transfer interaction (Shimazaki et al., 1997; Shimazaki et al., 1998), molecular recognition (Hong et al., 1993; Decher et al., 1994; Bourdillon et al., 1994; Lvov et al., 1995; Anzai et al., 1999), coordination interactions (Xiong et al., 1998), have been used as driving force for the multilayer buildup. In addition, layer-by-layer reactions have been also employed to construct robust multilayer thin films (Kohli et al., 1998; Major & Blanchard, 2001; Chan et al., 2002; Zhang et al., 2005; Such et al., 2006). Diversified building blocks have been used to construct LbL multilayer thin films, including polyelectrolytes (Kleinfeld & Ferguson, 1994), colloid and nanoparticles (Gao et al., 1994; Rogach et al., 2000; Fu et al., 2002a), dyes (Zhang et al.,1994; Sun et al., 1996), dendrimers (Zhang et al., 2003; Huo et al., 2003), clay minerals (Wei et al., 2007), carbon materials (Olek et al., 2004; Correa-Duarte et al., 2005), enzymes and proteins (Kong et al., 1994; Lvov & Moehwald, 2000; Sun et al., 2001), DNA (Lvov et al., 1993; Shchukin et al., 2004), viruses (Lvov et al., 1994) and so on. These building blocks can be fabricated into multilayer thin films simply by alternating deposition at liquid-solid interface, so-called conventional LbL assembly.

In order to fabricate single charged or water-insoluble building blocks, a series of unconventional LbL methods have been proposed. The key idea of these approaches includes more than one step in the assembly process, as shown in Figure 1. For example, the building blocks can self-assemble in solution to form molecular assemblies, and the molecular assemblies can be used as one of the building blocks subsequently for LbL assembly at liquid-solid interface. In this way, those building blocks which can not fabricated by conventional LbL assembly can be assembled by this unconventional LbL assembly. In addition, the unconventional LbL assembly can not only bring new structures but also endow the multilayer thin films with new functions (Zhang et al., 2007).
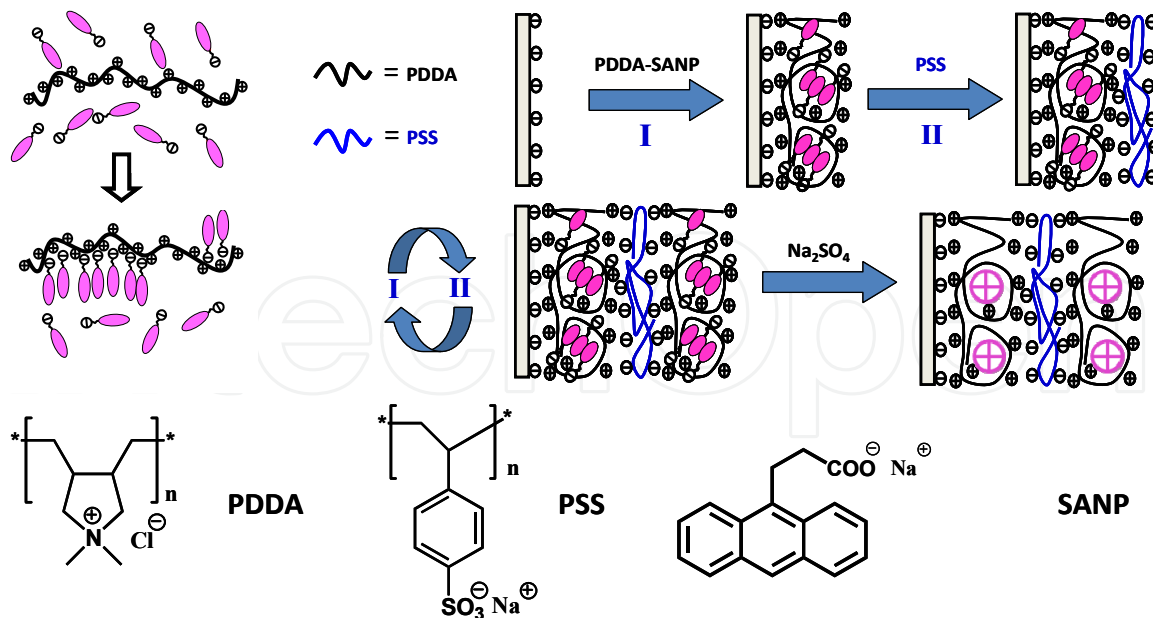
This chapter is to summarize different methods of unconventional LbL assembly, including electrostatic complex formation, hydrogen-bonded complex, block copolymer micelles and polymer-assisted complex. It will be noted that single charged or water-insoluble building blocks become self-assembling after these treatments in solution. When fabricating into multilayer thin films, this unconventional LbL assembly leads to development of new concept of surface imprinting, nanocontainers and nanoreactors.

Fig. 1. Schematic illustration of unconventional LbL assembly.

2. Electrostatic complex formation

An electrostatic complex for the fabrication of LbL films can be described as follows. First, polyelectrolytes are mixed with counter-charged molecules in aqueous solution to form electrostatic complex; second, the complex are deposited alternatively with counter-polyelectrolyte to form LbL films. Electrostatic complex formation is a convenient way to fabricate LbL films with embedded charged organic molecules, including single-charged or oligo-charged (Fabianowski et al., 1998; Chang-Yen et al., 2002; Das and Pal, 2002; Nicol et al., 2003; Chen et al., 2005).

One typical example is the incorporation of single charged molecules, e.g. sodium 9-anthracenepropionate (SANP) into LbL films (Chen et al., 2005), as shown in Figure 2. This negatively charged moiety is used to form a macromolecular complex with positively charged poly(diallyldimethylammonium chloride) (PDDA), PDDA–SANP in short, and multilayer films are fabricated by alternating deposition of the PDDA–SANP complex with poly(4-styrenesulfonate) (PSS) at the liquid-solid interface. It is well known that small molecules, such as SANP, can diffuse into conventional LbL films of PDDA/PSS. However, the amount of SANP assembled in this method is much larger than that in the diffusion method, and moreover, a controllable amount of SANP can be incorporated by adjusting the initial concentration of SANP in the PDDA–SANP complex solution.

Fig. 2. Schematic illustration of the incorporation of single charged SANP into LbL film.

Can LbL films act as a nanoreactor? To answer this question, the LbL film of PDDA-SANP/PSS is a nice model system, since anthracene moiety in SANP can undergo photo-cycloaddition under UV irradiation. As shown in Figure 3, the characteristic absorbance of anthracene between 250 and 425 nm decreases with UV irradiation, at the same time the absorbance of benzene around 205 nm increases, which indicates that SANP moieties incorporated in the LbL film undergo photocycloaddition to produce a photocyclomer. Interestingly, the quantum yield of photocycloaddition is about four times higher than that in the solution. The reason such photocycloaddition occurs with an enhanced quantum yield should be correlated with the aggregations of SANP in the LbL films which facilitates the reaction.
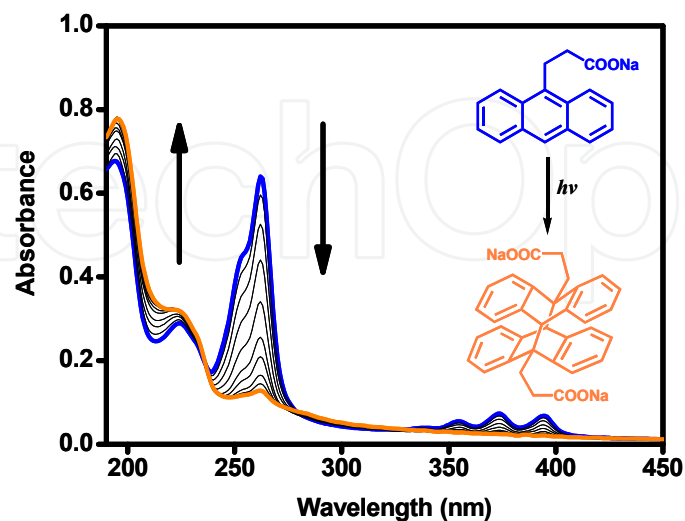
Fig. 3. Absorption spectra of PDDA-SANP/PSS multilayer film under UV irradiation for different times. Arrows indicate the transformation of the spectrum with increasing irradiation time.

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 an LbL film of PDDA–SANP/PSS into an aqueous solution of Na_2SO_4, the SANP can 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 control experiment, small molecules can diffuse into normal LbL films of PDDA/PSS, however, either positively charged or negatively charged species can be equally incorporated, indicative of no charge selectivity. In addition, the loading capacity of SANP in a PDDA–SANP/PSS film is seven times higher than that in a PDDA/PSS film. Therefore, the LbL films fabricated by this unconventional LbL method can be used as materials of permselectivity.

We are wondering if the above unconventional LbL method can be extended to incorporate positive charged building blocks and to fabricate films that are able to readsorb only positively charged moieties, whereas it repels negatively charged moieties. For this purpose, 1-pyrenemethylamine hydrochloride (PMAH) is chosen as a positive charged moiety (Chen et al., 2007). Similar to the previous discussion on SANP, PMAH can be incorporated into LbL films by the unconventional LbL method that involves the electrostatic complex formation of PMAH and PSS in solution and alternating deposition between the complex and PDDA at liquid-solid interface. When immersing the LbL films of (PDDA/PSS-PMAH)$_{10}$ into Na_2SO_4 aqueous solution of varying concentration, PMAH can be released from the LbL films and the releasing rate depends on the concentration of Na_2SO_4 solution. At a high Na_2SO_4 concentration of 0.62 mol/L, PMAH can be released completely in about 90 s. However, at a low concentration of 6.2×10^{-3} mol/L, it takes nearly 500s for the completely release of PMAH. Notably, the LbL films after releasing PMAH can selectively readsorb positively charged moiety while repelling the opposite.

Not all small molecules are suitable templates for fabrication of LbL films that can trap ion of one sign of charge while repelling the opposite. We have tried different cations and anions and realized that single-charged molecules bearing condensed aromatic structures are good candidates. The reasons are listed as following: (1) Single-charged molecules can form complexes with polyelectrolytes and also unbind easily, which is an important factor for successful incorporation into LbL films as we have mentioned above. Molecules with two or more charges can hardly unbind from the polyelectrolytes. (2) The small molecules we used in our experiment have a hydrophilic group and a hydrophobic group with condensed aromatic moiety. When forming a complex in aqueous solution, the aromatic hydrophobic groups might get together due to hydrophobic interaction as well as the π-π stacking interaction.

3. Hydrogen bonding complex

Hydrogen-bonded LbL assembly was first demonstrated by Rubner and our group simultaneously in 1997 (Stockton & Rubner, 1997; Wang et al., 1997; Wang et al., 2000). Since then, various building blocks have been fabricated into thin film materials on the basis of hydrogen bonding (Fu et al., 2002b; Zhang et al., 2003; Zhang et al., 2004; Zhang et al., 2007). This method is suitable for building blocks with hydrogen donors and acceptors, and it can

be feasible not only in the environment of aqueous solution but also in suitable organic solvent. Considering that hydrogen bonding is sensitive to environmental conditions, such as pH, the hydrogen-bonded LbL films can be erasable (Sukhishvili & Granick, 2000; Sukhishvili & Granick, 2002).

Inspired by the concept of unconventional LbL assembly, we attempt to develop unconventional method of LbL assembly on the basis of hydrogen bonding. It involves hydrogen-bonding complexation in solution and hydrogen-bonded LbL assembly at liquid-solid interface. The solvent used could be organic, which favors the formation of hydrogen-bonding. In this way, some water-insoluble small organic molecules can be loaded into multilayer thin films.

One of the examples of hydrogen-bonded unconventional LbL assembly is shown in Figure 4 (Zeng et al., 2007). First, a small organic molecule, bis-triazine (DTA) is mixed with poly(acrylic acid) (PAA) in methanol to form a hydrogen-bonding complex (PAA-DTA); second, LbL assembly is performed between the methanol solutions of PAA-DTA and diazo-resin (DAR), driven by hydrogen-bonding. In this way, DTA is loaded into the LbL film in a convenient and well-controlled manner. Since DAR is a photoreactive polycation, one can irradiate the film with UV light to convert the hydrogen bonding into covalent bond, therefore forming a stable multilayer film (Sun et al., 1998, 1999, 2000; Zhang et al., 2002).
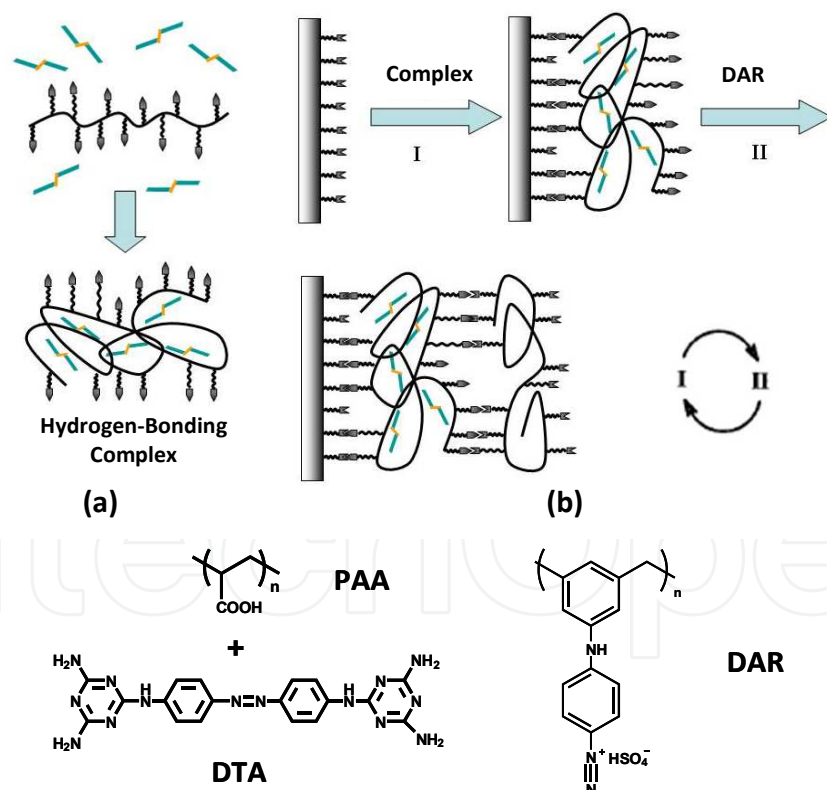
Fig. 4. Schematic illustration of hydrogen-bonded unconventional LbL assembly: Step 1, formation of hydrogen-bonding PAA-DTA complexes (a); Step 2, LbL assembly of PAA-DTA and DAR (b).

We have applied this method to a series of structurally related molecules with an increasing number of hydrogen bond donors and acceptors to find out the structural demand of the method. Our conclusion is only the molecules that can form multiple and strong hydrogen bonds with PAA are suitable for our method. One simple technique to test if molecules can interact with PAA strongly is described below: when mixing the molecules with PAA in solution, it means that there exist a strong interaction between the molecule and PAA if a floccule is formed. Therefore, those molecules are usually suitable for this unconventional LbL assembly.

4. Block copolymer micelles

Amphiphilic block copolymers are able to self-assemble into core–shell micellar structures in selective solvent. In order to take advantage of hydrophobic cores of the block copolymer micelles, we have 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 (Ma et al., 2005). As shown in Figure 5, 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. This is certainly another unconventional LbL assembly that involves micellar formation in solution and use of loaded micelles for LbL deposition at liquid-solid interface. In this way, small water-insoluble molecules can be fabricated.
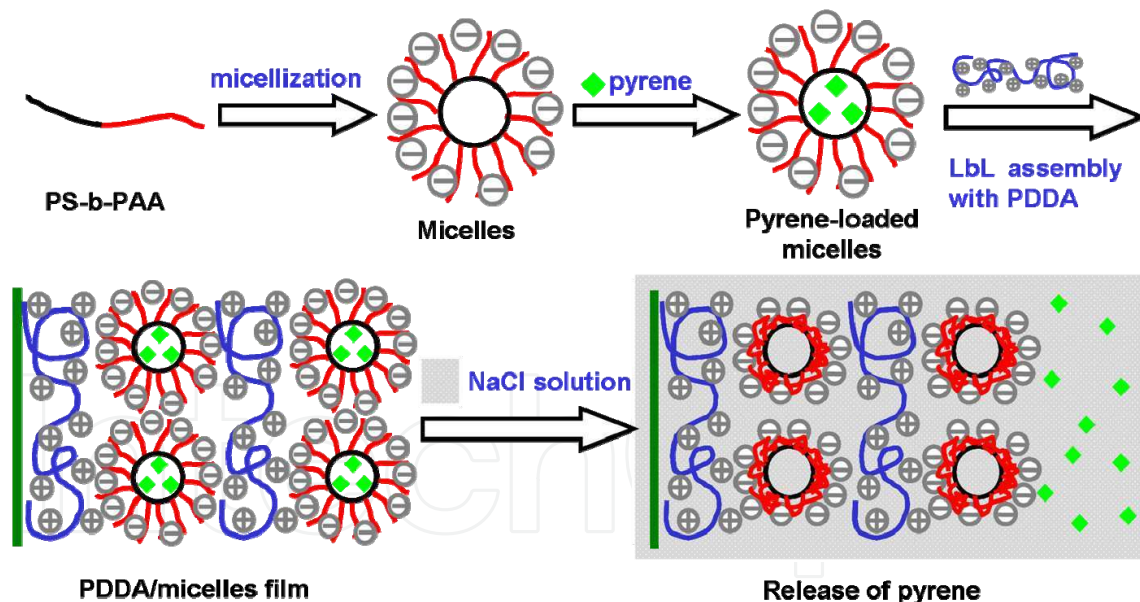
Fig. 5. Schematic illustration of the incorporation of pyrene into block copolymer micelles, LbL deposition of loaded micelles with PDDA, and the release of pyrene from the multilayer thin film.

The same concept can be extended to incorporate different water-insoluble molecules, such as azobenzene, for LbL assembly (Ma et al., 2006, 2007). 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 film 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 needs only several minutes, which is much faster than in normal solid films, but similar to that in dilute solutions, suggesting a way for enhancing the photophysical properties in the LbL films.

The above discussion concerns LbL films of block micelles when micelles are used to replace just one of the polyelectrolyte layers. The preparation of micelle-only multilayer is also possible. For this purpose, positively and negatively charged block copolymer micelles are needed as building blocks (Qi et al., 2006; Cho et al., 2006). For example, Block copolymer micelle/micelle multilayer films can be fabricated by alternating deposition of protonated poly(styrene-b-4-vinylpyrinde) and anionic poly(styrene-b-acrylic acid), as shown in Figure 6. The film growth is governed by electrostatic and hydrogen-bonding interactions between the block copolymer micelles. Multilayer films with antireflective and photochromic properties are obtained by incorporating water-insoluble photochromic (spiropyran) into the hydrophobic core (Cho et al., 2006). In addition, the micelle-only multilayer can be prepared not only on planar substrates but also on colloidal particulate substrates (Biggs et al., 2007).
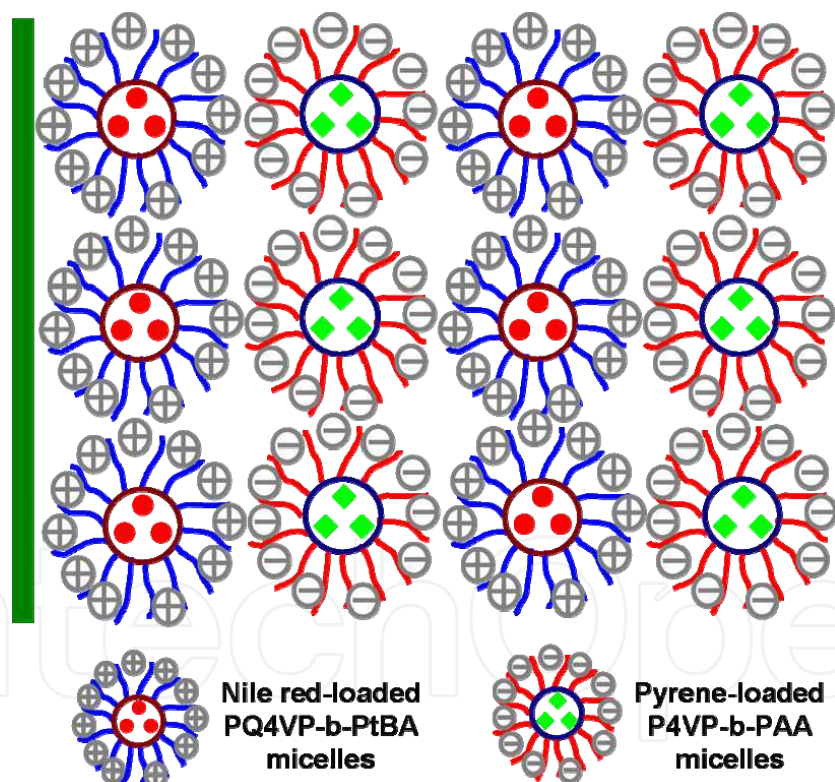
Fig. 6. Schematic illustration of LBL assembly of block copolymer micelle/micelle multilayer films with encapsulated guests.

The stability of micelles formed by low molecular weight surfactant is lower than block copolymer micelles, which usually cannot be used for LbL deposition. To improve the stability of micelles, a strategy is put forward that involves the use of polyelectrolyte to stabilize the micelles, which will be discussed in the following section.

5. Polymer-assisted complex

Polymer-assisted complex can be formed by the complexation of polymer with organic or inorganic components in solution through weak interaction such as electrostatic interactions, hydrogen-bonds, coordination interactions, guest-host interactions and so on. It has been demonstrated that diversified polymer-assisted complexes can be used as building blocks for the unconventional LbL assembly of multilayer thin films with well-tailored structures and functionalities, including polyelectrolyte-stabilized surfactant (Liu et al., 2008), polymeric complexes (Zhang & Sun, 2009; Liu et al., 2009; Guo et al., 2009), organic/inorganic hybrid complexes (Zhang et al., 2008).

Instead of using block copolymer micelles mentioned above as containers, Sun and co-workers found that the inexpensive polyelectrolyte-stabilized surfactant could be used as containers for noncharged species. For instance, they used this unconventional LbL assembly to realize the incorporation of noncharged pyrene molecules into multilayer films (Liu et al., 2008). First, noncharged pyrene molecules were encapsulated into the hydrophobic cores of the commonly used micelles formed by cetyltrimethylammonium bromide (CTAB); Second, the pyrene-loaded CTAB micelles were complexed with poly(acrylic acid) to obtain PAA-stabilized CTAB micelles, noted as PAA-(Py@CTAB), as shown in Figure 7; Then PAA-(Py@CTAB) were alternately deposited with PDDA through electrostatic interaction to produce PAA-(Py@CTAB)/PDDA multilayer thin film. As a consequence, pyrene molecules were firmly incorporated in the PAA-(Py@CTAB)/PDDA films with a high loading capacity. The assisted polymer plays an important role in stabilizing the micelles because CTAB micelles without assisted polymer can disassemble during the LbL deposition process. Considering that the surfactant micelles and polyelectrolytes are easily available, it is anticipated that this method can be extended to a wide range of polyelectroyte-stabilized surfactant micelles and will open a general and cost-effective avenue for the fabrication of advanced film materials containing noncharged species, such as organic molecules, nanoparticles and so forth by using LbL assembly technique.
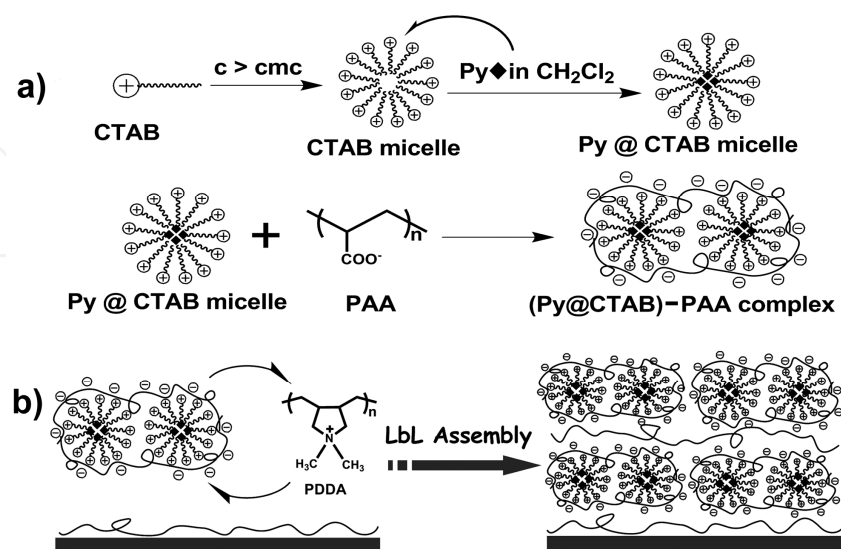

Fig. 7. (a) Preparative process of PAA-stabilized Py@CTAB micelles. (b) LbL deposition process for fabrication of PAA-(Py@CTAB)/PDDA multilayer films.

LbL assembled porous films could be hardly fabricated through conventional LbL assembly by directly alternate deposition of oppositely charged polyelectrolytes because of the flexibility of polyelectrolytes, which tends to close up any pre-designed pores and produce thin and compact films. However, by firstly preparing the polyelectrolyte complexes of negatively charged PAA and DAR (noted as PAA-DAR) and positively charged DAR and PSS (noted as DAR-PSS) as building blocks for further LbL assembly, a robust macroporous foam coating could be rapidly fabricated by direct LbL deposition of PAA-DAR and DAR-PSS complexes combined with subsequent photocross-linking (Zhang & Sun, 2009). These macroporous PAA-DAR/DAR-PSS foam coatings have a high loading capacity toward cationic dyes and can be used for dye removal from wastewater because of the large surface area and the abundance of negatively charged carboxylate and sulfonate groups provided by the foam coatings.

In addition of electrostatic interaction, hydrogen-bonded interaction could be also employed to form the polymer-assisted complex. For instance, poly(vinylpyrrolidione) (PVPON) and PAA could pe-assemble to polymeric complex through hydrogen-bonding interaction (denoted PVPON-PAA). Then, the pre-assembly complex could fabricate with poly(methacrylic acid) (PMAA) to a micrometre-thick PVPON-PAA/PMAA film with hierarchical micro- and nanostructures. After chemical vapor deposition of a layer of fluoroalkylsilane on top of the as-prepared multilayer thin film, superhydrophobic coatings were conveniently fabricated (Liu et al., 2009). The structure of the as-prepared PVPON-PAA/PMAA films could be well tailored by the mixing ratio of the PVPON-PAA complexes and the film preparative process. A non-drying LbL deposition process is critically important to realize the rapid fabrication of PVPON-PAA/PMAA films with hierarchical structures because the spherical structure of the PVPON&PAA complexes can be well preserved during film fabrication. In contrast, A N_2 drying step during LbL deposition process can produce a lateral shearing force, which produces thin and smooth films because of the spread and flattening of the PVPON-PAA complexes.
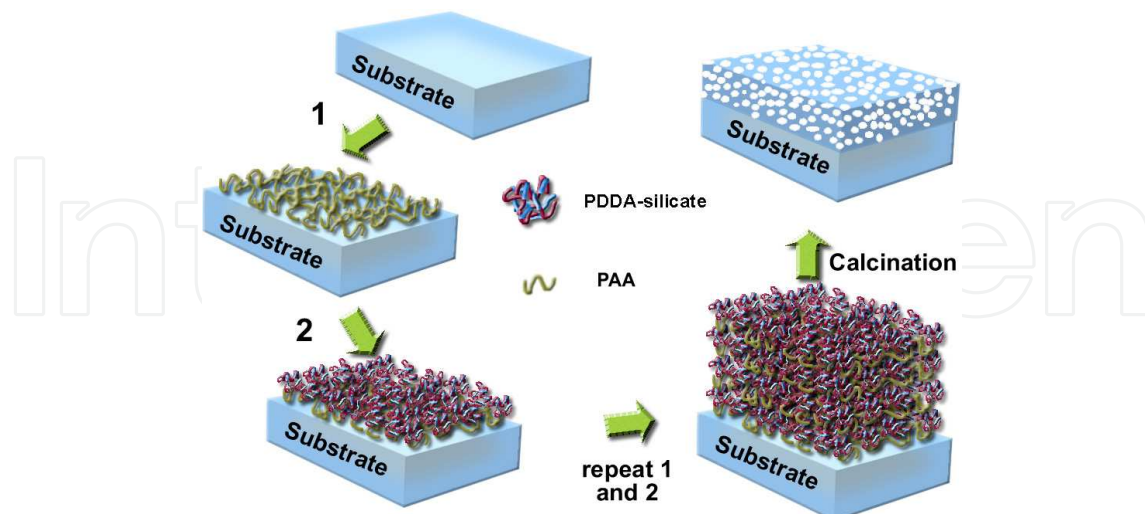

Fig. 8. Schematic illustration of the LbL deposition of PDDA-silicate complexes and PAA for fabrication of antireflection and antifogging coatings.

Besides polymeric complexes, polymer-assisted organic/inorganic hybrid complexes can be also assembled with counter species through unconventional electrostatic LbL assembly to

fabricate functional film materials. As shown in Figure 8, complexes of PDDA and sodium silicate (PDDA-silicate) were alternately deposited with PAA to fabricate PAA/PDDA-silicate multilayer thin films (Zhang et al., 2008). The removal of the organic components in the PAA/PDDA-silicate mulilayer films through calcination produces highly porous silica coatings with excellent mechanical stability and good adhesion to substrates. Quartz substrates covered with such porous silica coatings exhibit both antireflection and antifogging properties because of the reduced refractive index and superhydrophilicity of the resultant films. A maximum transmittance of 99.8% in the visible spectral range is achieved for the calcinated PAA/PDDA-silicate films deposited on quartz substrates. The use of PDDA-assisted silicate complexes instead of simplex sodium silicate can largely increase the ratio of the organic components in the LbL-deposited organic/inorganic hybrid films and therefore enhance the porosity of the calcinated films, which favors the fabrication of antireflection and antifogging coatings with enhanced performance.

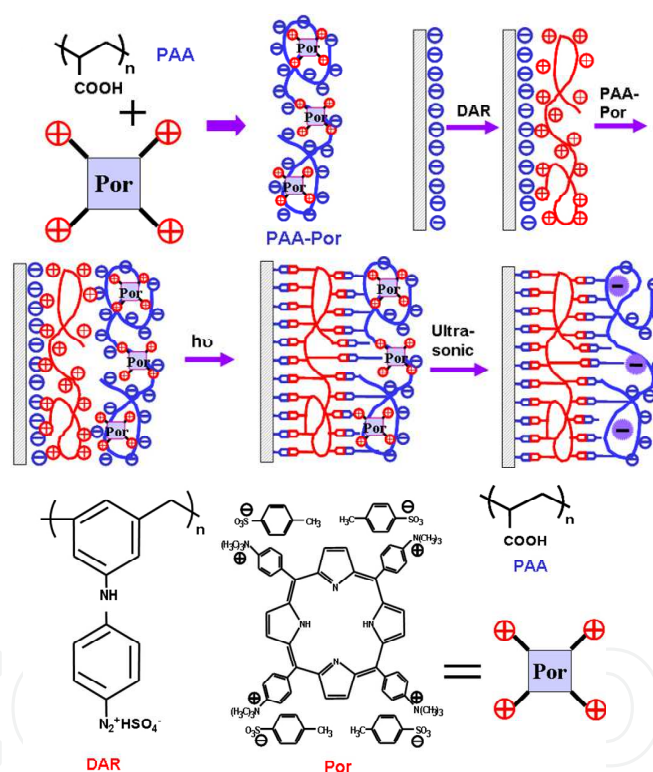## 6. Surface imprinting LbL film

Fig. 9. Schematic illustration of the formation of the imprinting complexes (PAA-Por) and the experimental procedure for the formation of surface imprints of multilayer thin film.

The unconventional LbL assembly is not only used for assembling building blocks which cannot be assembled by conventional method, but also for introducing new functions. Among them, surface imprinting in LbL nanostructured films is one typical example. It is well-known that molecularly imprinting polymers provide a general means to generate specific binding sites in polymer matrices (Wulff & Sarhan, 1972; Vlatakis et al., 1993; Zimmerman et al., 2002; Haupt & Mosbach, 2000; Wulff, 2002; Komiyama et al., 2002). However, they suffer from basic limitations associated with the limited concentration of

imprinted sites, and the bulk volume of the polymer matrices that requires long diffusion paths of the imprinted host molecules. In fact, a few previous reports have addressed the possibility of imprinting molecular-recognition sites in monolayer systems (Kempe et al., 1995; Lee et al. 1998; Lahav et al., 1999), but the effectiveness of these systems and their utility are limited. Surface imprinting LbL film can provide a solution to solve these problems, therefore opening a new avenue for surface imprinting with enhanced efficiency.

A general procedure for preparation of surface imprinting LbL films includes four steps. Taking the generation of imprinted sites for the porphyrin derivative (Por) as an example, as shown in Figure 9, firstly, an electrostatically stabilized complex between the positively charged porphyrin and PAA is formed in aqueous solution. Secondly, multilayer thin film is fabricated by alternating deposition of the complex PAA–Por and photoactive DAR. Thirdly, the layered structure is photo cross-linked to yield the covalent bridging of the layers by UV irradiation. In the final step, the template porphyrin molecules are washed off from the film to yield the surface imprinted matrix (Shi et al., 2007).
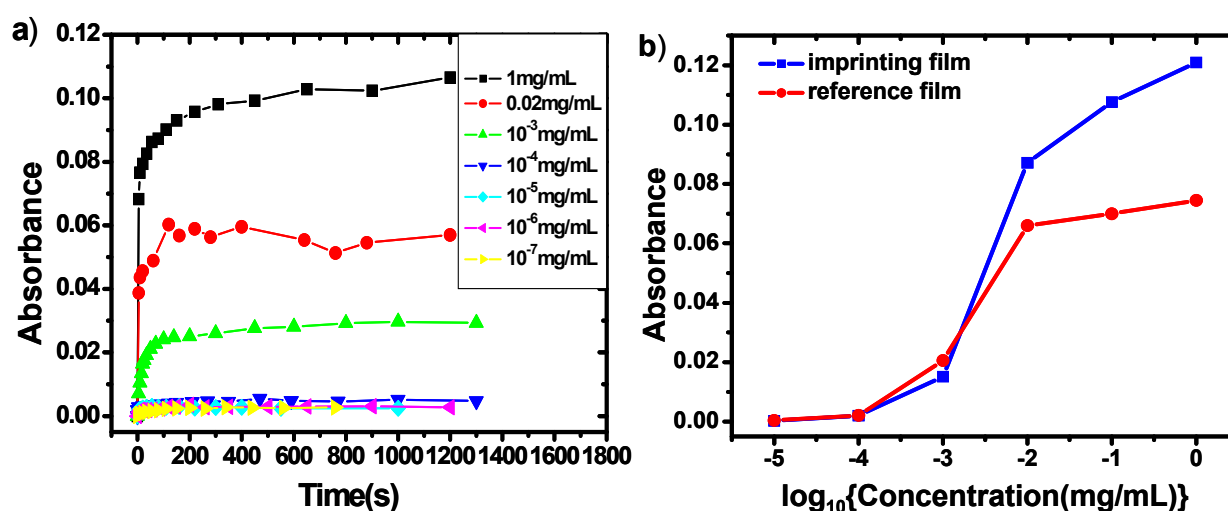

Fig. 10. a) Time-dependent absorbance of the Por association to the imprinted film at different bulk concentration of Por; b) Isothermal absorption curve of the Por relative to the imprinted film (blue curve) and the reference film (red curve).

The surface imprinting LbL films have advantage over other method in terms of thermodynamics and kinetics. As shown in Figure 10(a), the rate of binding of Por to the imprinted film is very fast, and the loading process reaches a saturation value at less than two min. Moreover, the absorbance of the saturation value of Por increases upon elevating the bulk concentration of Por, which indicates that the binding of Por is concentration-dependent. Furthermore, the formation of different saturation values for the absorbance of Por bound to the polymer at different bulk concentrations of Por implies that the association of Por is an equilibrium process. Knowing the saturation value of bound Por at different bulk concentrations, the binding constant of Por to the imprinted site is estimated to be 2×10^5 M^{-1}. The isothermal absorption is shown in Figure 10(b) by relating the absorbance of Por at 30 min against the concentration of Por. When the concentration of Por is lower than 10^{-2} mg mL^{-1}, the absorption of Por is similar in the imprinted film and the reference film. However, upon increasing the concentration of Por to 10^{-2} mg mL^{-1}, we observe that the imprinted film absorbs substantially more Por than the reference film.

Further support that the film binds the Por substrate to specific imprinted sites, rather than by sole electrostatic interactions, is obtained by the electrochemical probing of the association of the positively charged $Ru(NH_3)_6^{3+}$ label to the LbL film before and after exclusion of the template, Por, from the polymer. No redox response is observed for the $Ru(NH_3)_6^{3+}$ label when the polymeric film is loaded with the template Por, implying that the film insulates the interfacial electron transfer to the redox label, Figure 11(curve 1). Exclusion of the template results in the electrical response of $Ru(NH_3)_6^{3+}$, Figure 11(curve 2). That is, after exclusion of the template, the film is permeable to the redox label and the positively charged units bind to the negatively charged empty sites from which the Por is removed. Interaction of the $Ru(NH_3)_6^{3+}$ loaded polymer with the imprinted substrate, Por, results in a decrease in the electrical response of $Ru(NH_3)_6^{3+}$, implying that the redox label is competitively displaced by Por. That is, Por exhibits a substantially higher affinity for the polymer as compared to $Ru(NH_3)_6^{3+}$, Figure 11(curves 3 and 4). This is attributed to the fact that the imprinted sites in the film can sterically accommodate Por, in addition to its electrostatic stabilization by the negative charges associated with the polymer.
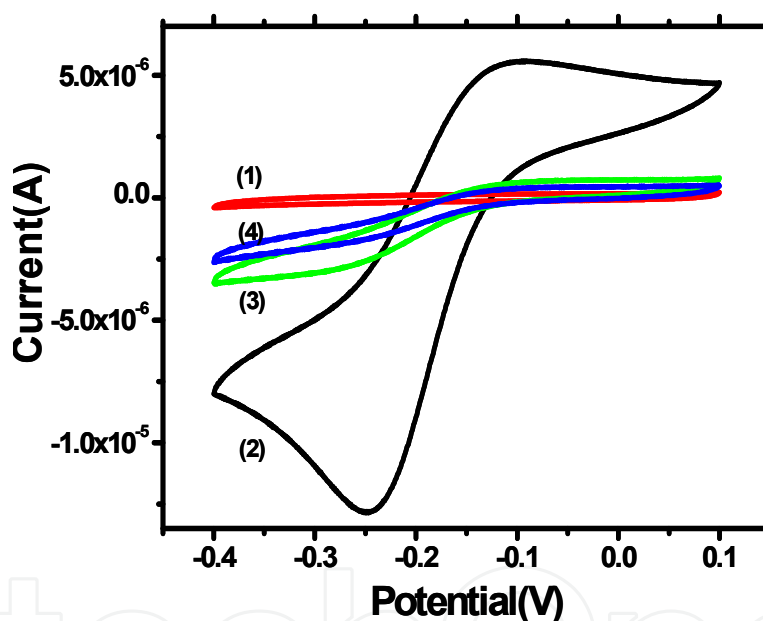

Fig. 11. Cyclic voltammograms of the gold electrodes modified by $(DAR/PAA–Por)_5DAR$ multilayer films in the presence of an electrolyte solution consisting of 3 mM $Ru(NH_3)_6^{3+}$ and 0.1 M KCl; 1) after UV irradiation and in the presence of bound Por; 2) removal of Por from the film by ultrasonic agitation in the ternary solution; 3, 4) after immersing the unloaded film in a mixed solution of 0.2 mgmL^{-1} Por, 2.4 mM $Ru(NH_3)_6^{3+}$,and 0.08 M KCl for 2 min and 20 min, respectively.

To improve the selectivity of surface imprinting LbL films, we have attempted to introduce the cooperativity of various specific interactions within the binding sites. We choose theophylline derivatives as the model template molecules to investigate the feasibility of our method in the fabrication of surface imprinting LbL films. Theophylline-7-acetic acid (THAA) is covalently conjugated to polyelectrolyte PAA with a cystamine bridge by amide linkage to form precursor assemblies PAAtheo15, which is a PAA with 15% of its carboxylic

acid grafted of THAA. The disulfide bond moiety of the cystamine bridge can introduce extra recognition sites as the thiol group obtained from reduction of disulfide is able to form hydrogen-bonding interactions with hydroxyl groups of the guest molecules. This additional mercapto recognition site, combined with the other hydrogen-bonding interactions established through template incorporation and film construction, renders selectivity for the nanostructured binding cavities in the LbL film (Niu et al., 2007; Niu et al., 2008).

7. Conclusions

The LbL assembly has experienced several stages of development: extension of various building blocks, LbL method driven by different driving forces, combination of layered nanoarchitectures and functional assemblies, and the unconventional LbL assembly as summarized and discussed in this chapter. In general, the unconventional LbL assembly includes supramolecular assembly in solution and LbL deposition at liquid-solid interface. Therefore, it can be regarded as one of the multi-level assembly. As you can see, the unconventional LbL method brings not only new supramolecular structures but also functions. However, 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.

8. References

Anzai, J.;Kobayashi, Y.; Nakamura, N.; Nishimura, M. & Hoshi, T. (1999). Layer-by-Layer construction of multilayer thin films composed of avidin and biotin-labeled Poly(amine)s. *Langmuir,* 1999, 15, 221-226.

Biggs, S.; Sakai, K.; Addison, T.; Schmid, A.; Armes, S. P.; Vamvakaki, M.; Bütün, V. & Webber, G. (2007). Layer-by-Layer formation of smart particle coatings using oppositely charged block copolymer micelles. *Adv. Mater.,* 2007, 19, 247–250.

Bourdillon, C.; Demaille, C.; Moiroux, J. & Savéant, J. M. (1994). Step-by-Step immunological construction of a fully active multilayer enzyme electrode. *J. Am. Chem. Soc.,* 1994, 116, 10328-10329.

Chan, E. W. L.; Lee, D. C.; Ng, M. K.; Wu, G. H.; Lee, K. Y. C. & Yu, L. P. (2002). A novel Layer-by-Layer approach to immobilization of polymers and nanoclusters. *J. Am. Chem. Soc.,* 2002, 124, 12238-12243.

Chang-Yen, A.; Lvov, Y.; McShane, M. J. & Gale, B. K. (2002). Electrostatic self-assembly of a ruthenium-based oxygen sensitive dye using polyion–dye interpolyelectrolyte formation. *Sens. Actuators, B,* 2002, 87, 336-345.

Chen, H.; Zeng, G. H.; Wang, Z. Q.; Zhang, X.; Peng, M. L.; Wu, L. Z. & Tung, C. H. (2005). To combine precursor assembly and Layer-by-layer deposition for incorporation of single-charged species: nanocontainers with charge-selectivity and nanoreactors. *Chem. Mater.,* 2005, 17, 6679-6685.

Chen, H.; Zeng, G. H.; Wang, Z. Q. & Zhang, X. (2007). To construct "ion traps" for enhancing the permselectivity and permeability of polyelectrolyte multilayer films. *Macromolecules,* 2007, 40, 653-660.

Cho, J.; Hong, J.; Char, K. & Caruso, F. (2006). Nanoporous block copolymer micelle/micelle multilayer films with dual optical properties. *J. Am. Chem. Soc.*, 2006, 128, 9935–9942.

Correa-Duarte, M. A.; Kosiorek, A.; Kandulski, W.; Giersig, M. &,Liz-Marzán, L. M. (2005). Layer-by-Layer assembly of multiwall carbon nanotubes on spherical colloids. *Chem. Mater.*, 2005, 17, 3268-3272.

Das, S. & Pal, A. J. (2002). Layer-by-Layer self-assembling of a low molecular weight organic material by different electrostatic adsorption processes. *Langmuir*, 2002, 18, 458-461.

Decher, G. & Hong, J. D. (1991a). Buildup of ultrathin multilayer films by a self-assembly process: I. Consecutive adsorption of anionic and cationic bipolar amphiphiles. *Makromol. Chem., Macromol. Symp.*, 1991, 46, 321-327.

Decher, G. & Hong, J. D. (1991b). Buildup of ultrathin multilayer films by a self-assembly process: II. Consecutive adsorption of anionic and cationic bipolar amphiphiles and polyelectrolytes on charged surfaces. *Ber. Bunsenges. Phys. Chem.*, 1991, 95, 1430-1434.

Decher, G.; Hong, J. D. & Schmitt, J. (1992). Buildup of ultrathin multilayer films by a self-assembly process: III. Consecutively alternating adsorption of anionic and cationic polyelectrolytes on charged surfaces. *Thin Solid Films*, 1992, 210/211, 831-835.

Decher, G.; Lehr, B.; Lowack, K.; Lvov, Y. & Schmitt, J. (1994). New nanocomposite films for biosensors: layer-by-layer adsorbed films of polyelectrolytes, proteins or DNA. *Biosens. Bioelectron.*, 1994, 9, 677-684.

Decher, G. (1997). Fuzzy nanoassemblies: toward layered polymeric multicomposites. *Science*, 1997, 277, 1232-1237.

Decher, G. & Schlenoff, J. B. (2002). *Multilayer Thin Films – Sequential Assembly of Nanocomposite Materials.* Wiley-VCH, Weinheim, Germany 2002.

Fabianowski, W.; Roszko, M. & Brodziñska, W. (1998). Optical sensor with active matrix built from polyelectrolytes–smart molecules mixture. *Thin Solid Films*, 1998, 327–329, 743- 747.

Fu, Y.; Xu, H.; Bai, S. L.; Qiu, D. L.; Sun, J. Q.; Wang, Z. Q. & Zhang, X. (2002a). Fabrication of a stable polyelectrolyte/Au nanoparticles multilayer film. *Macromol. Rapid Commun.*, 2002, 23, 256-259.

Fu, Y.; Chen, H.; Qiu, D. L.; Wang, Z. Q. & Zhang, X. (2002b) Multilayer assemblies of poly(4-vinylpyridine) and poly(acrylic acid) bearing photoisomeric spironaphthoxazine via hydrogen bonding. *Langmuir*, 2002, 18, 4989-4995.

Gao, M. Y.; Gao, M. L.; Zhang, X.; Yang, Y.; Yang, B. & Shen, J. C. (1994). Constructing PbI_2 nanoparticles into a multilayer structure using the molecular deposition (MD) method. *J. Chem. Soc., Chem. Commun.*, 1994, 2777-2778.

Guo, Y. M.; Geng, W. & Sun, J. Q. (2009). Layer-by-layer deposition of polyelectrolyte-polyelectrolyte complexes for multilayer film fabrication. *Langmuir*, 2009, 25, 1004-1010.

Hammond, P. T. (2004). Form and function in multilayer assembly: new applications at the nanoscale. *Adv. Mater.*, 2004, 16, 1271–1293.

Haupt, K. & Mosbach, K. (2000). Molecularly imprinted polymers and their use in biomimetic sensors. *Chem. Rev.*, 2000, 100, 2495–2504.

Hong, J. D.; Lowack, K.; Schmitt, J. & Decher G. (1993). Layer-by-layer deposited multilayer assemblies of polyelectrolytes and proteins: From ultrathin films to protein arrays. *Prog. Colloid Polym. Sci.,* 1993, 93, 98-102.

Huo, F. W.; Xu, H. P.; Zhang, L.; Fu, Y.; Wang, Z. Q. & Zhang, X. (2003). Hydrogen-bonding based multilayer assemblies by self-deposition of dendrimer. *Chem. Commun.,* 2003, 874-875.

Iler, R. K. (1966). Multilayers of colloidal particles. *J. Colloid Interface Sci.,* 1966, 21(6), 569-594.

Kempe, M.; Glad, M. & Mosbach, K. (1995). An approach towards surface imprinting using the enzyme ribonuclease A. *J. Mol. Recognition,* 1995, 8, 35-39.

Kleinfeld, E. R. and Ferguson, G. S. (1994). Stepwise formation of multilayered nanostructural films from macromolecular precursors. *Science,* 1994, 265, 370-373.

Kohli, P.; Taylor, K. K.; Harris, J. J. & Blanchard, G. J. (1998). Assembly of covalently-coupled disulfide multilayers on gold. *J. Am. Chem. Soc.,* 1998, 120, 11962-11968.

Komiyama, M.; Takeuchi, T.; Mukawa, T. & Asanuma, H. (2002). *Molecular Imprinting.* Wiley-VCH, Weinheim, Germany 2002.

Kong, W.; Zhang, X.; Gao, M. L.; Zhou, H.; Li, W. & Shen, J. C. (1994). A new kind of immobilized enzyme multilayer based on cationic and anionic interaction. *Macromol. Rapid Commun.,* 1994, 15, 405-409.

Lahav, M.; Katz, E.; Doron, A.; Patolsky, F. & Willner, I. (1999). Photochemical imprint of molecular recognition sites in monolayers assembled on Au electrodes. *J. Am. Chem. Soc.,* 1999, 121, 862–863.

Lee, S. W.; Ichinose, I. & Kunitake, T. (1998). Molecular imprinting of azobenzene carboxylic acid on a TiO_2 ultrathin film by the surface sol-gel process. *Langmuir,* 1998, 14, 2857-2863.

Liu, X. K.; Zhou, L.; Geng, W. & Sun, J. Q. (2008). Layer-by-layer-assembled multilayer films of polyelectrolyte-stabilized surfactant micelles for the incorporation of noncharged organic dyes. *Langmuir,* 2008, 24, 12986-12989.

Liu, X. K.; Dai, B. Y.; Zhou, L. & Sun, J. Q. (2009). Polymeric complexes as building blocks for rapid fabrication of layer-by-layer assembled multilayer films and their application as superhydrophobic coatings. *J. Mater. Chem.,* 2009, 19, 497–504.

Lvov, Y.; Decher, G. & Sukhorukov, G. (1993). Assembly of thin films by means of successive deposition of alternate layers of DNA and poly(allylamine). *Macromolecules,* 1993, 26, 5396–5399.

Lvov, Y.; Haas, H.; Decher, G. & Möhwald, H. (1994). Successive deposition of alternate layers of polyelectrolytes and a charged virus. *Langmuir,* 1994, 10, 4232-4236.

Lvov, Y.; Ariga, K.; Ichinose, I. & Kunitake, T. (1995). Layer-by-layer architectures of concanavalin A by means of electrostatic and biospecific interactions. *J. Chem. Soc., Chem. Commun.,* 1995, 2313-2314.

Lvov, Y. & Moehwald, H. (2000). *Protein Architectures: Interfacing Molecular Assemblies and Immobilization Biotechnology,* Marcel Dekker, New York 2000.

Ma, N.; Zhang, H. Y.; Song, B.; Wang, Z. Q. & Zhang, X. (2005). Polymer micelles as building blocks for Layer-by-Layer assembly: an approach for incorporation and controlled release of water-insoluble dyes. *Chem. Mater.,* 2005, 17, 5065-5069.

Ma, N.; Wang, Y. P.; Wang, Z. Q. & Zhang, X. (2006). Polymer micelles as building blocks for the incorporation of azobenzene: enhancing the photochromic properties in Layer-by-Layer films. *Langmuir*, 2006, 22, 3906-3909.

Ma, N.; Wang, Y. P.; Wang, B. Y.; Wang, Z. Q.; Zhang, X.; Wang, G. & Zhao, Y. (2007). Interaction between block copolymer micelles and azobenzene-containing surfactants: from coassembly in water to Layer-by-Layer assembly at the interface. *Langmuir,* 2007, 23, 2874-2878

Major, J. S. & Blanchard, G. J. (2001). Covalently bound polymer multilayers for efficient metal ion sorption. *Langmuir*, 2001, 17, 1163-1168.

Nicol, E.; Habib-Jiwan, J. L. & Jonas, A. M. (2003). Polyelectrolyte multilayers as nanocontainers for functional hydrophilic molecules. *Langmuir,* 2003, 19, 6178-6186.

Niu, J.; Shi, F.; Liu, Z.; Wang, Z. Q. & Zhang, X. (2007). Reversible disulfide cross-linking in Layer-by-Layer films: preassembly enhanced loading and pH/reductant dually controllable release. *Langmuir,* 2007, 23, 6377-6384.

Niu, J.; Liu, Z. H.; Fu, L.; Shi, F.; Ma, H. W.; Ozaki, Y. & Zhang, X. (2008). Surface imprinted nanostructured layer-by-layer film for molecular recognition of theophylline–derivatives. *Langmuir,* 2008, 24, 11988–11994.

Olek, M.; Ostrander, J.; Jurga, S,; Moehwald, H.; Kotov, N.; Kempa, K. & Giersig, M. (2004). Layer-by-layer assembled composites from multiwall carbon nanotubes with different morphologies. *Nano Lett.,* 2004, 4, 1889-1895.

Qi, B.; Tong, X. & Zhao, Y. (2006). Layer-by-Layer assembly of two different polymer micelles with polycation and polyanion coronas. *Macromolecules*, 2006, 39, 5714-5719.

Rogach, A. L.; Koktysh, D. S.; Harrison, M. & Kotov, N. A. (2000). Layer-by-Layer assembled films of HgTe nanocrystals with strong infrared emission. *Chem. Mater.,* 2000, 12, 1526–1528.

Shchukin, D. G.; Patel, A. A.; Sukhorukov, G. B. & Lvov, Y. M. (2004). Nanoassembly of biodegradable microcapsules for DNA encasing. *J. Am. Chem. Soc.,* 2004, 126, 3374-3375.

Shi, F.; Liu, Z.; Wu, G. L.; Zhang, M.; Chen, H.; Wang, Z. Q. & Zhang, X. (2007). Surface imprinting in Layer-by-Layer nanostructured films. *Adv. Funct. Mater.* 2007, 17, 1821–1827.

Shimazaki, Y.; Mitsuishi, M.; Ito, S. & Yamamoto, M. (1997). Preparation of the Layer-by-Layer deposited ultrathin film based on the charge-transfer interaction. *Langmuir,* 1997, 13, 1385-1387.

Shimazaki, Y.; Mitsuishi, M.; Ito, S. & Yamamoto, M. (1998). Preparation and characterization of the Layer-by-Layer deposited ultrathin film based on the charge-transfer interaction in organic solvents. *Langmuir,* 1998, 14, 2768-2773.

Stockton, W. B. & Rubner, M. F. (1997). Molecular-level processing of conjugated polymers. 4. Layer-by-Layer manipulation of polyaniline via hydrogen-bonding interactions. *Macromolecules,* 1997, 30, 2717-2725.

Such, G. K.; Quinn, J. F.; Quinn, A.; Tjipto, E. & Caruso, F. (2006). Assembly of ultrathin polymer multilayer films by click chemistry. *J. Am. Chem. Soc.,* 2006, 128, 9318-9319.

Sukhishvili, S. A. & Granick, S. (2000). Layered, erasable, ultrathin polymer films. *J. Am. Chem. Soc.,* 2000, 122, 9550–9551.

Sukhishvili, S. A. & Granick, S. (2002). Layered, erasable polymer multilayers formed by hydrogen-bonded sequential self-assembly. *Macromolecules,* 2002, 35, 301–310.

Sun, Y. P.; Zhang, X.; Sun, C. Q.; Wang, Z. Q.; Shen, J. C.; Wang, D. J. & Li, T. L. (1996). Supramolecular assembly of alternating porphyrin and phthalocyanine layers based on electrostatic interactions. *Chem. Commun.*, 1996, 2379-2380.

Sun, J. Q.; Wu, T.; Sun, Y. P.; Wang, Z. Q.; Zhang, X.; Shen, J. C. & Cao, W. X. (1998). Fabrication of a covalently attached multilayer via photolysis of layer-by-layer self-assembled films containing diazo-resins. *Chem. Commun.*, 1998, 1853-1854.

Sun, J. Q.; Wang, Z. Q.; Sun, Y. P.; Zhang, X. & Shen, J. C. (1999). Covalently attached multilayer assemblies of diazo-resins and porphyrins. *Chem. Commun.*, 1999, 693-694.

Sun, J. Q.; Cheng, L.; Liu, F.; Dong, S. J.; Wang, Z. Q.; Zhang, X. & Shen, J. C. (2000). Covalently attached multilayer assemblies containing photoreactive diazo-resins and conducting polyaniline. *Colloids Surf., A,* 2000, 169, 209-217.

Sun, J. Q.; Sun, Y. P.; Wang, Z. Q.; Sun, C. Q.; Wang, Y.; Zhang, X. & Shen, J. C. (2001). Ionic self-assembly of glucose oxidase with polycation bearing Os complex. *Macromol. Chem. Phys.*, 2001, 202, 111-116.

Vlatakis, G.; Andersson, L. I.; Müller, R. & Mosbach, K. (1993). Drug assay using antibody mimics made by molecular imprinting. *Nature*, 1993, 361, 645 – 647.

Wang, L. Y.; Wang, Z. Q.; Zhang, X. & Shen, J. C. (1997). A new approach for the fabrication of an alternating multilayer film of poly(4-vinylpyridine) and poly(acrylic acid) based on hydrogen bonding. *Macromol. Rapid Commun.*, 1997, 18, 509-514.

Wang, L. Y.; Cui, S. X.; Wang, Z. Q.; Zhang, X.; Jiang, M.; Chi, L. F. & Fuchs, H. (2000). Multilayer assemblies of copolymer PSOH and PVP on the basis of hydrogen bonding. *Langmuir,* 2000, 16, 10490-10494.

Wei, H.; Ma, N.; Shi, F. Wang, Z. Q. & Zhang, X. (2007). Artificial nacre by alternating preparation of Layer-by-Layer polymer films and $CaCO_3$ strata. *Chem. Mater.*, 2007, 19, 1974-1978.

Wulff, G & Sarhan, A. (1972). Use of polymers with enzyme-analgous structures for the resolution of raeemates. *Angew. Chem. Int. Ed. Engl,* 1972, 11, 341-344.

Wulff G. (2002). Enzyme-like catalysis by molecularly imprinted polymers. *Chem. Rev.,* 2002, 102, 1–28.

Xiong, H. M.; Cheng, M. H.; Zhou, Z.; Zhang, X. & Shen, J. C. (1998). A new approach to the fabrication of a self-organizing film of heterostructured polymer/Cu_2S nanoparticles. *Adv. Mater.*, 1998, 10, 529-532.

Zeng, G. H.; Gao, J.; Chen, S. L.; Chen, H.; Wang, Z. Q. & Zhang, X. (2007). Combining hydrogen-bonding complexation in solution and hydrogen-bonding-directed Layer-by-Layer assembly for the controlled loading of a small organic molecule into multilayer films. *Langmuir,* 2007, 23, 11631-11636.

Zhang, X.; Gao, M. L.; Kong, X. X.; Sun, Y. P. & Shen, J. C. (1994). Build-up of a new type of ultrathin film of porphyrin and phthalocyanine based on cationic and anionic electrostatic attraction. *J. Chem. Soc. Chem. Commun.*, 1994, 1055-1056.

Zhang, X. & Shen, J.C. (1999). Self-Assembled ultrathin films: from layered nanoarchitectures to functional assemblies. *Adv. Mater.*, 1999, 11, 1139–1143.

Zhang, X.; Wu, T.; Sun, J. Q. & Shen, J. C. (2002). Ways for fabricating stable layer-by-layer self-assemblies:combined ionic self-assembly and post chemical reaction. *Colloids Surf., A*, 2002, 198–200, 439-442.

Zhang, H. Y.; Fu, Y.; Wang, D.; Wang, L. Y.; Wang, Z. Q. & Zhang, X. (2003). Hydrogen-bonding-directed Layer-by-Layer assembly of dendrimer and poly(4-vinylpyridine) and micropore formation by post-base treatment. *Langmuir,* 2003, 19, 8497-8502.

Zhang, H. Y.; Wang, Z. Q.; Zhang, Y. Q. & Zhang, X. (2004). Hydrogen-bonding-directed Layer-by-Layer assembly of poly(4-vinylpyridine) and poly(4-vinylphenol): effect of solvent composition on multilayer buildup. *Langmuir,* 2004, 20, 9366-9370.

Zhang, F.; Jia, Z. & Srinivasan, M. P. (2005). Application of direct covalent molecular assembly in the fabrication of polyimide ultrathin films. *Langmuir,* 2005, 21, 3389-3395.

Zhang, X.; Chen, H & Zhang, H. Y. (2007). Layer-by-layer assembly: from conventional to unconventional methods. *Chem. Commun.,* 2007, 1395-1405.

Zhang, L. B.; Yang, L.; Sun, J. Q. & Shen, J. C. (2008). Mechanically stable antireflection and antifogging coatings fabricated by the layer-by-layer deposition process and postcalcination. *Langmuir,* 2008, 24, 10851-10857.

Zhang, L. & Sun, J. Q. (2009). Layer-by-layer deposition of polyelectrolyte complexes for the fabrication of foam coatings with high loading capacity. *Chem. Commun.,* 2009, 3901–3903.

Zimmerman, S. C.; Wendland, M. S.; Rakow, N. A.; Zharov, I. & Suslick, K. S. (2002). Synthetic hosts by monomolecular imprinting inside dendrimers. *Nature,* 2002, 418, 399-403.

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This book provides a timely overview of a current state of knowledge of the use of polymer thin film for important technological applications. Polymer thin film book covers the scientific principles and technologies that are necessary to implement the use of polymer electronic device. A wide-ranging and definitive coverage of this emerging field is provided for both academic and practicing scientists. The book is intended to enable readers with a specific background, e.g. polymer nanotechnology, to become acquainted with other specialist aspects of this multidisciplinary field. Part A of the book covers the fundamental of the key aspect related to the development and improvement of polymer thin film technology and part B covers more advanced aspects of the technology are dealt with nano-polymer layer which provide an up-to-date survey of current research directions in the area of polymer thin film and its application skills.

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