

IONIC SELF-ASSEMBLY AND HUMIDITY SENSITIVITY OF POLYELECTROLYTE MULTILAYERS*

Hai-hu Yu** and De-sheng Jiang

Fiber Optic Sensing Technology Center, Wuhan University of Technology, Wuhan 430070, China

Abstract Multilayer thin films of alternately adsorbed layers of polyelectrolytes PDPA and PS-119 were formed on both planar silica substrates and optical fibers through the ionic self-assembly technique. Intrinsic Fabry-Perot cavities were fabricated by stepwise assembling the polyelectrolytes onto the ends of optical fibers for the purposes of fiber optical device and sensor development. Ionically assembled polyelectrolyte multilayer thin films, in which there are hydrophilic side groups with strong affinity towards water molecules, are a category of humidity-sensitive functional materials. The polyelectrolyte multilayer thin film Fabry-Perot cavity-type fiber optical humidity sensor can work over a wide range from about 0% RH to about 100% RH with a response time less than 1 s.

Keywords Ionic self-assembly, Polyelectrolyte, Multilayer thin film, Humidity, Fabry-Perot interferometer, Fiber optical sensor

INTRODUCTION

Organic thin films are of great interest in many applications such as electro-optic device fabrication, sensor development and surface modification engineering. A number of techniques, including spin coating, the Langmuir-Blodgett (L-B) method^[1] and so on, have been used by many authors to form functional thin-layered materials. Applications of organic thin films in electro-optic devices and sensors usually require the control of microscopic architecture of thin films to obtain desired macroscopic properties. For this reason, the L-B method and self-assembly techniques^[2] have received much attention because both of them can be used to produce densely packed and well-defined layered materials with layer thickness controllable on the nanometer scale. However, precursor molecules suitable for L-B transfer are limited, and the need for strict control of the surface pressure, the temperature and the dipping speed makes it very difficult to handle. Moreover, L-B multilayers are held together mainly by van der Waals forces, which makes the supramolecular systems mechanically unstable.

Self-assembly strategies have many advantages over the L-B method. The adsorption process from solutions is much simpler than L-B transfer and not restricted by the shape and size of the substrate. The covalent bonds or ionic attraction between the layers endow the multilayers with higher stability than their L-B counterparts. Unfortunately, the chemisorption self-assembly process, by which covalent bindings between the layers can be achieved, is time-consuming for multilayer thin film fabrication. Physisorption self-assembly, i.e. ionic self-assembly, is a quick process because the Coulombic interaction between oppositely charged molecules is easier than the chemical activation during the chemisorption process. The fabrication of charged inorganic colloid multilayers via physisorption was first described by Iler in 1966^[3]. In the early 1990s Decher and his co-workers extended Iler's work to fabricate multilayers of polyions and composite layered materials^[4-6]. For the ionic self-assembly technique, large numbers of precursor molecules are available; the alternating adsorption process is

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** Corresponding author: Hai-hu Yu (余海湖), E-mail: hhyu@wutos.com

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effective even for multilayer adsorption; no complicated instrument or strict operation conditions are required. Because of these characteristics, this technique has been used to assemble ordered multilayers of polyelectrolytes, inorganic colloidal particles, metal colloidal clusters, biological macromolecules and so on^[7-10]. Ionically self-assembled functional multilayer thin films, *e.g.* conducting multilayers^[11], heterostructure electroluminescent diodes^[12], non-linear optical thin films^[13], *etc.*, have been reported by different authors.

In the last two decades, we have witnessed tremendous growth in fiber optical communications and sensing. Continued demands of novel devices, materials and technology for applications in fiber optical communication and sensing have opened up many opportunities for scientists in opto-electronics, chemistry, and materials science. Studies of functional coatings on optical fibers for optical communication and sensing are being carried out all over the world. Sol-gel process, sputtering technique, vapor deposition, *etc.*, have been used by some authors to coat thin films on optical fibers^[14-16]. However, in the sol-gel process, it is difficult to control the thickness of the films; in the sputtering technique or vapor deposition process, it is rather inconvenient to make thin films of alternate materials. The ionic self-assembly technique characteristically places little restriction on substrates, making it possible to build up multilayer thin films on optical fibers in an effective way.

Polyelectrolytes are water-soluble polymers with charged side groups and exhibit inherent affinity to polar molecules. The adsorption of water molecules on polyelectrolyte multilayers raises concern about two aspects. One is to consider the fabrication, storage and application of the polyelectrolyte multilayer surfaced components or devices. The other is the design of novel humidity sensors. The monitoring of the humidity of air is widely required in many fields, and the development of humidity sensors with high performance has been an interesting area of research for a long time. Electronic humidity sensors have been extensively used as a well-established tool for many years. However, in some circumstances, the measurement of humidity using fiber optical sensors is desirable and, on the other hand, optical sensors can offer many advantages over conventional electronic sensors^[17]. So, it is interesting to build up ionic self-assembled polyelectrolyte thin films onto optical fibers and study the behaviors of polyelectrolyte thin films in a varying humidity environment.

In the present paper, we described our work pertinent to the ionic self-assemblies of polyelectrolytes on both planar substrates and optical fibers, and reported our experimental results on the humidity sensitivity of the polyelectrolyte multilayer thin films by using a fiber optical measurement arrangement.

EXPERIMENTAL

Poly(diallyldimethylammonium chloride) (PDDA; $M_w = 400,000-500,000$) was obtained from Aldrich and polymeric dye poly s-119 (PS-119; $M_w = 70,000$ (ca.)) was available from Sigma. They were used without further purification. Ultrapure water with a resistivity of $\sim 18 \text{ M}\Omega \cdot \text{cm}$ was obtained by using a Barnstead Nanopure water purification system. An aqueous solution of PDDA of $1 \times 10^{-2} \text{ mol/L}$ based on the monomeric repeating unit was prepared by diluting the PDDA (20 wt%) solution with pure water to the designed concentration. An aqueous solution of PS-119 of 2 mg/mL was prepared by dissolving PS-119 powder in pure water with vigorous stirring. The substrates, including silica glass slides and optical fibers, were cleaned and negatively charged in a mixed solution of 30% hydrogen peroxide and concentrated sulfuric acid in a volume ratio of 3:7, thoroughly rinsed with pure water and dried in a nitrogen stream. All glassware was cleaned in caustic ethanol solution, thoroughly rinsed with water and dried prior to use.

Polyelectrolyte multilayers were fabricated in a clean room at ambient temperature according to the following procedure. A charged silica slide or an optical fiber was first dipped into the unstirred PDDA solution in an open beaker for 3 min and thoroughly washed with pure water. Then, the PDDA masked substrate was dipped into the PS-119 solution for 3 min and washed with pure water again. The above procedure was repeated cyclically until a PDDA/PS-119 multilayer thin film of desired bilayer number was deposited onto the planar substrate or the end face of the optical fiber.

The monitoring of the deposition of PDDA/PS-119 multilayers onto the end faces of optical fibers and the investigation on the sensitivity behaviors of the polyelectrolyte multilayer thin films with respect to the relative humidity of air were carried out on an experimental setup schematically illustrated in Fig. 1. The experimental

setup consisted of several essential parts, including monomode optical fibers, a light-emitting diode (LED), a fused tapered 2×2 coupler and a photodetector. An amplifier and a recorder were also used but are not shown in the figure. The monomode optical fiber had a core diameter of $9 \mu\text{m}$ and a cladding diameter of $125 \mu\text{m}$, respectively; the LED had a wavelength of $1.3 \mu\text{m}$ and the coupler had a coupling ratio of 50:50 at this wavelength at room temperature. The photodetector was used to detect the optical signals reflected from the thin film-coated end face of an optical fiber. After depositing every two bilayers of PDDA/PS-119 onto the end face of an optical fiber, the reflected light intensity was measured. In each measurement, the thin film-coated optical fiber was placed inside a plastic bottle half-filled with silica-gel desiccant, and the system was allowed to stand for a while to reach its equilibrium. The silica gel was used to provide a stable humidity environment for the thin film-coated optical fiber during optical measurement. Humidity sensitivity measurements were carried out under the following conditions. Different fixed relative humidity levels were created by using several saturated solutions of salts including $\text{LiCl} \cdot \text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NaCl , KCl , K_2SO_4 . Silica-gel desiccant was still used. The presumption was that the humidity of the air in the plastic bottle half-filled with silica-gel desiccant was about 0% RH. The plastic bottles containing salt solutions and silica gel were placed in a temperature-tunable water-bath to control the temperature as required. The humidity levels created in this way should inherently have an error of $\pm 2\%$. We investigated the humidity sensitivity of PDDA/PS-119 multilayers by placing the thin film-coated optical fibers inside the plastic bottles and measuring the reflected light intensity at different humidity levels. PDDA/PS-119 multilayer assemblies and optical measurements were carried out at 25°C .

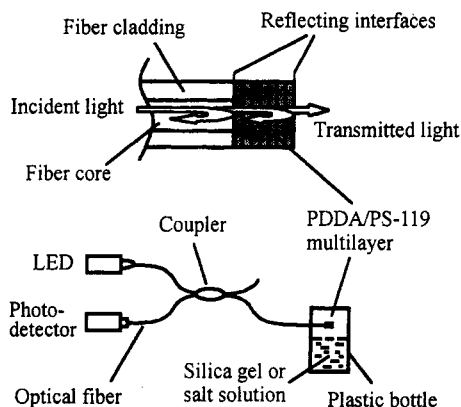


Fig. 1 Schematic diagram of experimental setup for monitoring the deposition of PDDA/PS-119 multilayer assembled onto optical fibers and illustration of assembled multilayer at the end of an optical fiber

RESULTS AND DISCUSSION

The chemical structures of the monomeric repeating units of PDDA and PS-119 are showed in Fig. 2. Both PDDA and PS-119 are strong electrolytes. As a result, in a wide pH range, both polyions will possess some net charges due to dissociation and will experience strong electrostatic attraction between the opposite charges during the assembling process. The assembled layer sequence of a PDDA/PS-119 multilayer is schematically illustrated also in Fig. 2. When a negatively charged substrate, *e.g.* a silica slide or an optical fiber, was dipped into the solution of PDDA, some of the positively charged quaternary ammonium groups were attracted by the ionic forces toward the substrate. Because the polymer chains are flexible, they were bent in response to these forces and the substrate was thus masked by a monolayer of PDDA molecules. On the PDDA monolayer-coated substrate, the rest of the positively charged quaternary ammonium groups formed a net positively charged distribution on the outermost surface. When the positively charged surface was dipped into the PS-119 solution, a PS-119 monolayer was attracted and fixed onto the PDDA monolayer-masked surface. By repeating this process,

a PDDA and PS-119 alternate multilayer was formed. UV-Vis spectroscopy is a powerful tool for monitoring the growth process of a polyelectrolyte multilayer thin film. The absorbance spectra following the assembly process of a PDDA/PS-119 multilayer on a silica slide are shown in Fig. 3. The spectra show that the PDDA/PS-119 multilayers exhibit characteristic absorption between 350 nm and 600 nm and have an absorbance maximum at 480 nm. From Fig. 4, we can find that there is a linear dependence of the absorbance at 480 nm on the bilayer number. The linear increment in the absorbance with respect to the number of bilayers suggests that the alternating adsorption of the polyelectrolytes is stepwise and that the multilayer deposition in layer-by-layer fashion brings an equal amount of materials to the substrate at each assembly cycle.

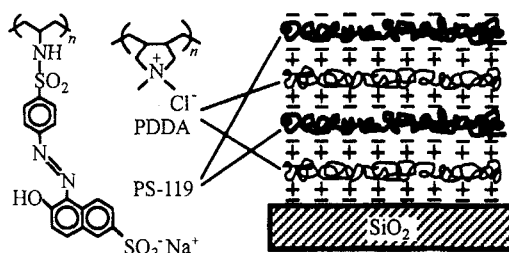


Fig. 2 Chemical structures of PDDA and PS-119 and schematic illustration of a polyelectrolyte multilayer fabricated on a silica substrate by using the ionic self-assembly technique

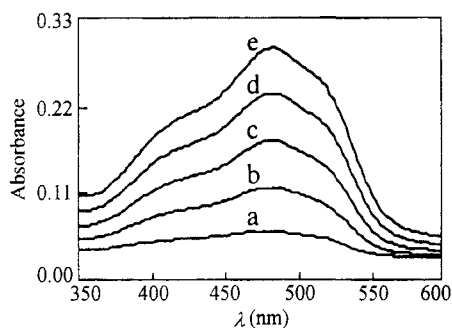


Fig. 3 Optical absorbance spectra of PDDA/PS-119 multilayers on silica substrates
The curves marked with a, b, c, d and e correspond to the spectra of 5-, 10-, 15-, 20- and 25-bilayer multilayers.

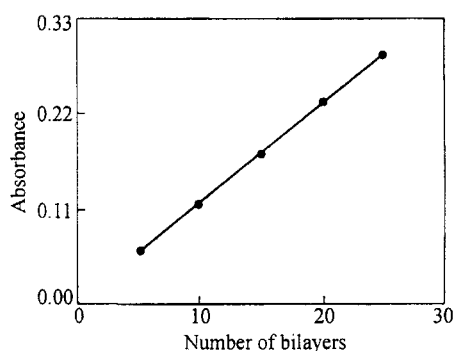


Fig. 4 Dependence of the absorbance at 480 nm on the number of PDDA/PS-119 bilayers

After depositing every two bilayers of PDDA/PS-119 onto the end face of an optical fiber under the same condition as applied to silica slides, we placed the coated fiber into a plastic bottle containing silica gel desiccant at 25°C and measured the reflected light intensity. Figure 5 shows the curve of the reflected light intensity detected by the photodetector against the number of bilayers. From our early results of small-angle X-ray reflectivity measurements on PDDA/PS-119 multilayers^[18], we know that the contrast of electron density between layer PDDA and layer PS-119 is very small and that the PDDA/PS-119 multilayer thin film is “homogeneous”. Therefore, although the multilayer consisted of alternate layers of PDDA and PS-119, we can treat the PDDA/PS-119 thin film as a single layer coating. Obviously, after a PDDA/PS-119 multilayer was deposited onto an optical fiber, two reflecting interfaces were created at the end of the optical fiber. One reflecting interface is the optical fiber/multilayer interface, and the other one is the multilayer/air interface. The light incident from the optical fiber into the polyelectrolyte thin film will experience refraction and reflection as if within a single

layer coating. The optical fiber and the multilayer thin film constituted an intrinsic optical fiber Fabry-Perot (F-P) interferometer with low fineness, of which the multilayer thin film was the F-P cavity. Some authors have described the mathematical expression of the reflected light power for an F-P cavity^[19]. Here we would like to conduct a general discussion according to the principle of optics^[20]. If no optical absorption and scattering are involved and if the incident light is normal to the thin film, the reflected light intensity output of a single layer coating is directly proportional to the reflectance of the thin film and the reflectance of the thin film can be expressed as:

$$R = \frac{(n_2 - n_0)^2 \cos^2 \frac{\delta}{2} + \left(\frac{n_0 n_2}{n_1} - n_1\right)^2 \sin^2 \frac{\delta}{2}}{(n_0 + n_2) \cos^2 \frac{\delta}{2} + \left(\frac{n_0 n_2}{n_1} + n_1\right)^2 \sin^2 \frac{\delta}{2}} \quad (1)$$

where n_0 is the refractive index of air, n_1 is the refractive index of the multilayer thin film, n_2 is the refractive index of the substrate, *i.e.* the optical fiber in our case, and δ is the phase difference of any two sequential light beams reflected at the two reflecting interfaces. As the incident light is normal to the thin film, the phase difference can be expressed as:

$$\delta = \frac{4\pi n_1 d}{\lambda} \quad (2)$$

where λ is the wavelength of the incident light, and d is the thickness of the multilayer thin film. During optical measurement, we placed the thin film coating in a humidity-constant environment. So the refractive index of the thin film is a constant and the phase difference is a function of thickness of the thin film. Because the dipping process is consistent, each dipping cycle will add a bilayer of equal thickness to the thin film. As a result, the phase difference is a function of the bilayer number of the multilayer, and, hence, the reflectance of the thin film is a function of the bilayer number of the multilayer. Therefore, on the basis of the above general deduction, we can know that, as the number of bilayers is increased, the thickness of the thin film is increased, and the phase difference of the two sequential reflected light beams is consequently subject to modulation. In response to the phase modulation, the reflectance of the thin film or the light intensity reflected by the thin film will experience oscillation. This oscillation can be observed from the curve in Fig. 5. The oscillation of the curve depicts the interferometric nature of the multilayer thin film optical fiber F-P cavity. This result shows that, using the ionic self-assembly process, multilayer thin films of alternate materials with controlled layer sequence can be formed on optical fibers in an effective way, and novel fiber optical devices, such as F-P filters or reflectors and F-P cavity-based sensors could be developed. On the other hand, from this reflected intensity versus bilayer number curve, we can know that, if the adsorption process is consistent, the reflected intensity will change smoothly as the number of bilayers increases. So, the simple fiber optical experimental setup described in the paper may be used instead of a UV-Vis spectrometer to monitor the stepwise growth of polyelectrolyte multilayers in some cases.

Before depositing polyelectrolyte thin films onto optical fibers, we placed the uncoated fibers in different humidity environments to measure the reflected light intensity, but no obvious change was observed. However, after depositing thin films onto the fibers, pronounced changes can be observed. The results of thin films of different bilayers in different humidity environments are shown in Fig. 6. For any one of the curves in this figure, the reflected light intensity of a thin film F-P cavity decreases as the humidity increases from about 0% RH to 97% RH and the slope of all the curves at higher RH is steeper than that between 0% RH and 80% RH. These phenomena show that the multilayer thin films are susceptible to humidity. This humidity sensitivity of the thin films results from the adsorption of water molecules onto the polyelectrolyte multilayers. In the polyelectrolyte multilayers, there are many hydrophilic $-\text{SO}_3^-$ and quaternary ammonium side groups, which exhibit strong affinity to water molecules. At certain temperature and pressure, the adsorption and desorption of water vapor on a multilayer thin film will reach a dynamic equilibrium. Because of the adsorption of water molecules, the

refractive index of the polyelectrolyte thin film will decrease, and the thickness of the film will increase. However, from our experiment we find that, when the number of bilayers in the multilayer is less than about 50, the adsorption of water molecules has a much stronger effect on the refractive index than on the thickness of a thin film. At higher humidity, more water molecules will be adsorbed onto the polyelectrolyte multilayer and the refractive index of the multilayer thin film will decrease to a larger extent. According to the principles of optics, we know that, as the refractive index of a thin film decreases, the reflectance will decline. Because of this, we can observe in Fig. 6 that the reflected intensity decreases with increasing humidity. At RH levels above 80%, water molecular clusters will be formed in the thin film. The water molecular clusters will greatly decrease the refractive index of the thin film, which results in a steeper slope and a deviation from the linearity of intensity-humidity curves. In our work, it was found that at a wavelength of $1.3\ \mu\text{m}$, we can get the steepest slope and very good linearity at 40 bilayers. So, 40-bilayer thickness is optimal for humidity sensor designs.

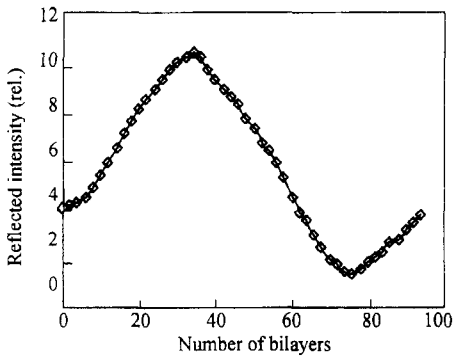


Fig. 5 Reflected light intensity as a function of the number of PDDA/PS-119 bilayers

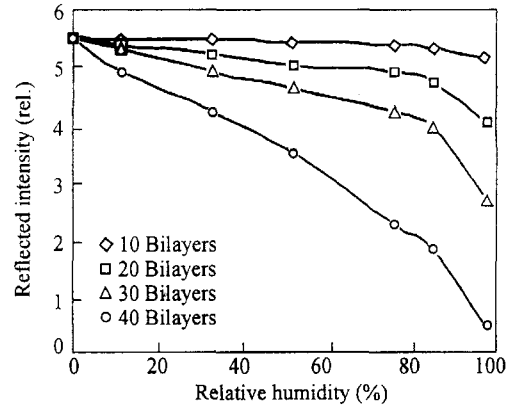


Fig. 6 Reflected light intensity as a function of relative humidity in air

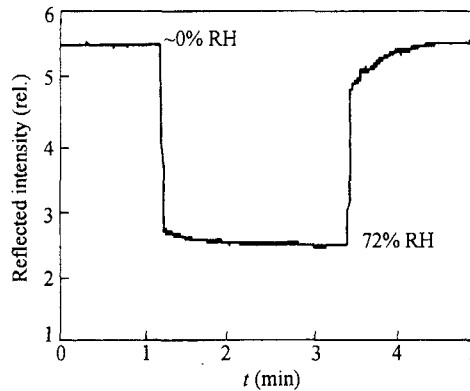


Fig. 7 Response curve for a fiber optical F-P interferometric humidity sensor based on a 40-bilayer polyelectrolyte multilayer thin film

Figure 7 depicts the typical response curve for a polyelectrolyte multilayer thin film F-P cavity-typed fiber optical humidity sensor. When a sensor head of 40-bilayer thin film was transferred from dry air into a humid environment, the reflected intensity output reached a stable value within 1 s. Conversely, when the sensor was transferred from water vapor-containing air into dry air, the signal rapidly decayed back to the baseline. Because the thickness of a thin film with several tens of bilayers is very small, the diffusion of water vapor in the multilayer thin film can reach the terminal in a short time, and a dynamic equilibrium between the adsorption and

desorption of water vapor on the thin film can be quickly established. The quick establishment of the adsorption/desorption equilibrium offers the humidity sensor with excellent response time. We found that, with such an excellent response time, this sensing system can follow human breathing very well. Because it can be made by the ionic self-assembly process at low cost, the sensor head for monitoring human breathing may be designed as a disposable part.

CONCLUSIONS

Uniform polyelectrolyte multilayers can be formed on planar substrates and on optical fibers by using the ionic self-assembly technique. The growth of polyelectrolyte multilayers on the solid surfaces is stepwise and consistent during the dipping process. Intrinsic optical fiber F-P interferometers can be made by stepwise assembling polyelectrolytes onto the end faces of optical fibers. The F-P interference phenomenon can be observed on the reflected intensity-bilayer number oscillogram. The result suggests that novel fiber optical devices, such as F-P filters or reflectors, and F-P cavity-based fiber optical sensors might be developed through this approach in an effective way.

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