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Self-assembly of polyaniline/polyacrylic acid films via acid–base reaction induced deposition

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Abstract

The layer-by-layer self-assembly of polyaniline (PAN) and polyacrylic acid (PAA) has been accomplished via the alternate spontaneous adsorption of base-type PAN from its dilute *N*-methylpyrrolidinone solution and PAA from its aqueous solution based on the acid–base reaction of PAN and PAA. The thickness of the films can be manipulated at nanometer scale by the concentration of PAN solution and recycling times. It is found that the PAN base film cannot be doped to emeraldine salt by PAA in the presence of ammonium persulfate. The UV–Vis spectroscopy was used to characterize the self-assembling process and the oxidation states of PAN. The electrochemical cyclic voltammetric and electrochromic properties of the self-assembled films were also studied. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Self-assembly; Polyaniline; Polyacrylic acid

1. Introduction

Polyaniline (PAN) is now regarded as one of the most technologically promising electrically conductive polymers due to its ease of synthesis, low cost, versatile processibility and relatively stable electrical conductivity. Ultrathin films of PAN has received great interest in recent years due to its potential applications in transparent electrodes, chemical and biological sensors, chemically modified electrodes and other solid state and molecular electronic devices [1–3]. Recently, the ultrathin self-assembled layer of PAN has been used to control the charge injection and electroluminescence efficiency in polymer light-emitting diodes [4]. In addition, interesting new effects may take place in very thin films compared to bulk samples [5].

Langmuir–Blodgett (LB) technique has been widely used to fabricate various ultrathin films, including PAN films [6]. Self-assembling (SA) is another promising technique to fabricate ultrathin films and has been extensively developed in recent years to prepare various multilayers including polyelectrolytes, metal colloids, inorganic semiconductor nanoparticulates, intercalative compounds, biological molecules, dyes, fullerenes, conducting polymers, and light-emitting polymers [7]. Compared with the LB technique, the latter method has at least three advantages: (1) the substrate can have any form; (2) deposition time is independent of the substrate area; and (3) the method can be used in the laboratory without special equipment such as the LB thoughs [8].

Recently Rubner's group has obtained a serials of PAN ultrathin films via layer-by-layer SA technique based on electrostatic interaction or hydrogen bonding [9,10]. In their procedure, aqueous solution of acid-doped PAN was used. However, doped PAN was susceptible to aggregation and precipitation, and the solution can be used for about only 1 h. Thus, a lot of PAN will be wasted. In addition, the existence of the small molecule acid dopants in the resulted films may make the electrical stability become poor [11].

PAN base can be doped by polymeric acids [11]. We have successfully fabricated self-assembled PAN/poly(styrene-sulfonic acid)(PSSA) films with small molecule dopants free utilizing the doping reaction of PAN and PSSA [12]. The PAN solution can be used all the time as PAN base has relatively good solubility in *N*-methylpyrrolidinone (NMP) and its dilute solution is stable at room temperature. Some differences appeared when the technique was used to prepare PAN/Polyacrylic acid (PAA) self-assembled films. In the present article, we report our research results on SA of PAN/PAA films.

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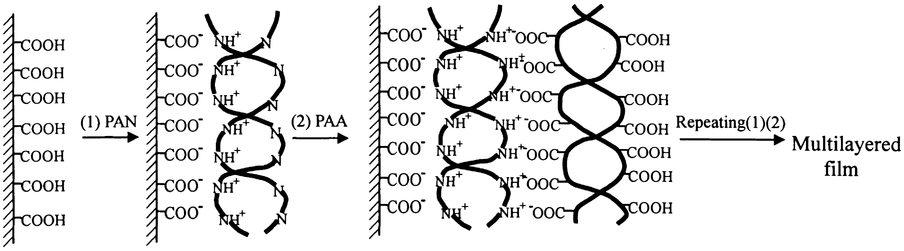

Fig. 1. The schematic diagram of layer-by-layer SA of PAN/PAA films.

2. Experimental

PAN was prepared and purified according to the procedure similar to Ref. [13], using $(NH_4)_2S_2O_8$ as an initiator. The solution of PAN base was prepared by dissolving the polymer powder in NMP, vigorously stirred, and filtered before use. 0.1% PAN solution was used in our experiment unless specially stated. Poly(diallyldimethylammoniumchloride)(P^+) with high molecular weight was used as received from Aldrich. PAA was synthesized by the polymerization of acrylic acid initiated by $(NH_4)_2S_2O_8$ and the remained $(NH_4)_2S_2O_8$ was removed by adding small amount of hydroquinone into the resulted PAA solution or standing the solution for several months. Other used chemicals are of chemical or analytical grade.

Quartz, glass and ITO glass slides were used as substrates for optical absorption, electrical conductivity, and electrochromism measurement, respectively. These substrates were firstly treated by a hot H_2SO_4/H_2O_2(7:3) bath for 1 h, sonicated in ultrapure water for 10 min, and thoroughly rinsed with water. Platinum line was used for electrochemical study, which was cleaned according to the conventional method. The positively charged substrates were obtained according to the procedure of Fendler et al. [14] by immersing the substrates in 1% P^+ aqueous solution for 20 min and rinsed by water. After dried by compressed air, these substrates were immersed in PAA solution for 10 min, and a monolayer of PAA can be absorbed on the surface via electrostatic interaction [7].

The construction of PAN/PAA multilayer involved the following steps: (1) the substrates treated as mentioned before were immersed in PAN solution for 10 min, rinsed with *N*, *N*-dimethylformamide (DMF), dried with compressed air; (2) immersed in PAA solution for 15 min, rinsed with pure water and dried. Repeating (1) and (2) led to multilayered films. The schematic diagram of the process is shown in Fig. 1.

The oxidation states of PAN and the relative thickness of the films were studied by their UV–Vis spectra, which was recorded on the Beijing Eraic UV-1100 spectrometer. The electrochemical experiments were performed in a three-electrode cell, using a platinum line of 0.47 mm diameter as working electrode, a platinum line as counter electrode and a saturated calomel electrode (SCE) as reference at

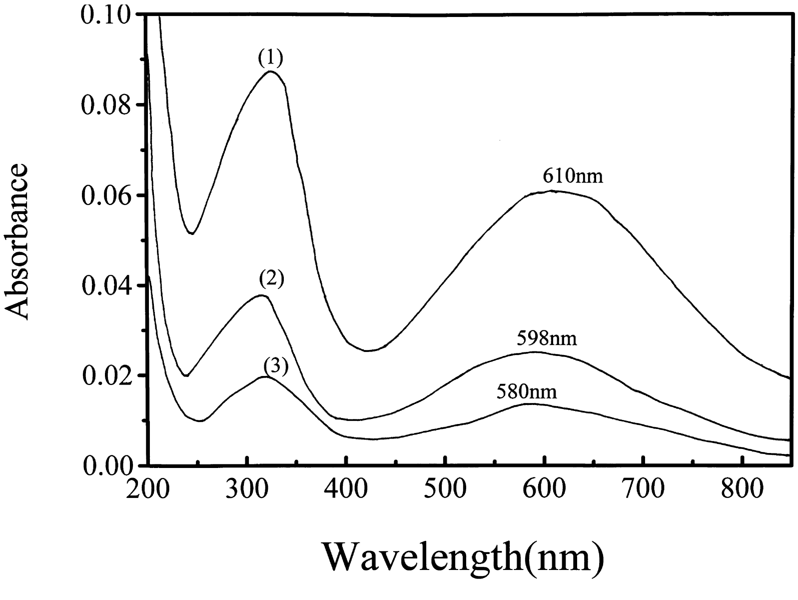

Fig. 2. The UV–Vis spectra of single monolayers of PAN prepared by SA process from PAN solution with various concentrations: (1) 0.2%; (2) 0.1%; (3) 0.05%.

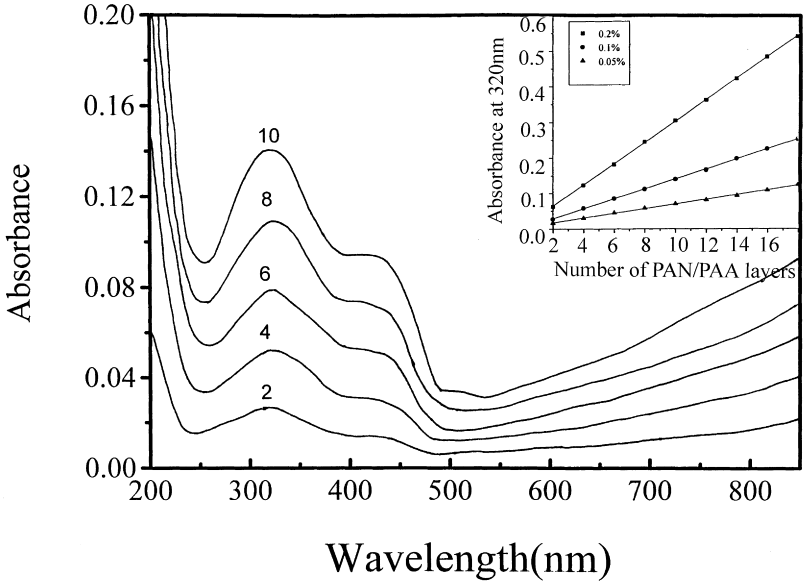

Fig. 3. The UV–Vis spectra of PAN/PAA multilayered films with various number of bilayers (each bilayer was always terminated with PAA and the concentration of the PAN solution was 0.1%). The inset shows how the absorbance at 320 nm increases with the number of bilayers for various PAN solutions with different concentrations.

room temperature. Cyclic voltammetry was performed on Jingke weak electric current analyzer at the scanning rate of 50 m V S^{-1} between −0.2 and 0.8 V.

3. Results and discussions

3.1. Assembly of single monolayers of PAN film

As shown in Fig. 1, when the substrate with carboxylic acid group was immersed in PAN solution, a monolayer of PAN base was absorbed onto the surface as the result of the acid–base reaction between PAN base and carboxylic acid. From the UV–Vis spectra of the resulted film shown in Fig. 2, we can find that the UV–Vis spectra of the absorbed PAN are in agreement with that of the emeraldine base, indicating that the absorbed PAN is not doped. This is imaginable as the amount of PAA absorbed on the substrate surface is as thick as several nanometers and its molecular chains are greatly fixed on the surface due to the electrostatic interaction between PAA and P^+. Only the carboxylic acid group in the outside surface took part in the reaction.

As shown in Fig. 2, the absorbed amount of PAN on the substrate increased with the increase of the solution

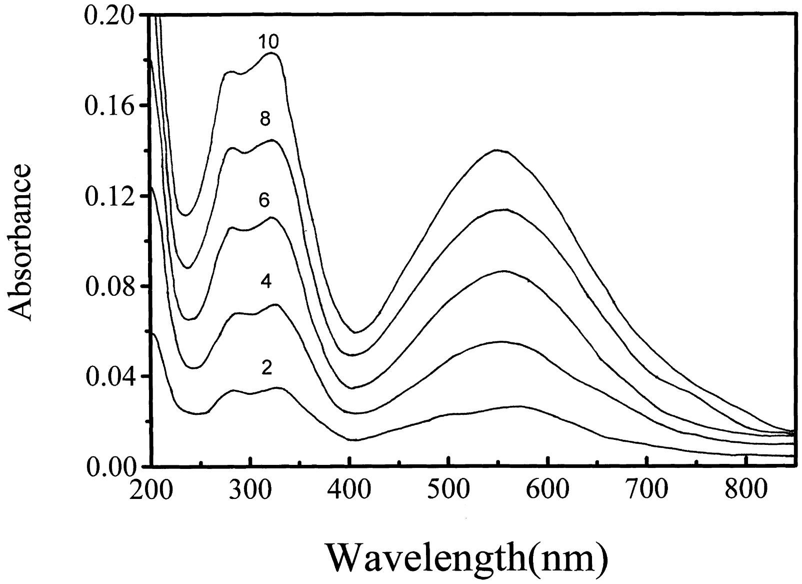

Fig. 4. The UV–Vis spectra of PAN/PAA multilayered films with various number of bilayers prepared in the presence of 0.03% ammonium persulfate.

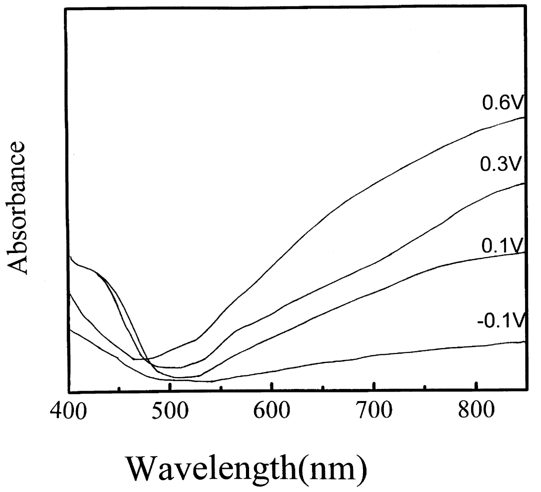

Fig. 5. The visible absorption spectra of PAN/PAA film at various potentials. 0.5 M H_2SO_4 aqueous solution was used as electrolyte. The absorbance of ITO glass was included.

concentration of PAN. Based on the absorbance data of the self-assembled film and the relationship of the thickness and the absorbance of PAN film in the literature [10], we estimate that the thickness of the films assembled from 0.05, 0.1 and 0.2% PAN solution are approximately 2, 5 and 11 nm, respectively.

Interestingly, the exciton absorption band at ~600 nm in the UV–Vis spectra of the assembled film is affected by the thickness of the film. The absorption peaks are located at 580, 598 and 610 nm, respectively, for the films with different thickness. The blue shift of the absorption peaks with the decrease of dimension may be due to the quantum effect of nanostructured materials. Otherwise, the oxidation state of PAN film is thickness dependent. The phenomenon was also observed in the self-assembled PSSA/PAN film [12].

3.2. Assembly of multilayered PAN films

The as-prepared PAN monolayers could be doped by PAA if the film was subsequently immersed into PAA solution. Its UV–Vis spectra after treated by PAA are shown in Fig. 3, which are in agreement with that of emeraldine salt. The result of the doping reaction did not only lead to the change of PAN from the insulating state to the conductive state, but also induced the deposition of another monolayer of PAA molecule and made the surface become acid again (see Fig. 1). Such surface can absorb another monolayer of PAN if the substrate was immersed in PAN solution again. Alternately immersed the substrate in PAN and PAA solutions, a green multilayered film of PAN/PAA can be obtained.

The thickness of the films can be controlled by assembling the times and the PAN solution concentration. As shown in Fig. 3, the absorbance of the film increased linearly with the increase of number of PAN/PAA, indicating that the absorbed materials in each cycle are equivalent.

3.3. Effect of $(NH_4)_2S_2O_8$ on the oxidation state of PAN

When an oxidant, $(NH_4)_2S_2O_8$, was included in PAA solution(e.g. in the newly polymerized PAA solution), the properties of the resulted film are different from that systems without $(NH_4)_2S_2O_8$ added. As demonstrated by their UV–Vis spectra in Fig. 4, the PAN base film obtained in step (1) cannot be doped to emeraldine salt if the base film was immersed into PAA($(NH_4)_2S_2O_8$)solution. The PAA solution with 0.03% $(NH_4)_2S_2O_8$ was used in our experiment. The resulting film is pale purple and their spectra is similar to that of nigraniline [15] indicating that the PAN was not doped by PAA, but oxidized to a higher oxidation state by $(NH_4)_2S_2O_8$; even the $(NH_4)_2S_2O_8$ concentration was very small. Some authors have reported that the emeraldine base can be directly oxidized to high intrinsic oxidation states by $(NH_4)_2S_2O_8$ in the absence of an acid [15]. We found that the oxidation process can also take place in the presence of some weak organic acids. The effect of ammonium persulfate on the doping process of PAN implies that the self-assembled PAN films with various oxidation states may be conveniently obtained by simply adjusting the chemistry of assembling solutions. There has been no report on the preparation of ultrathin nigraniline films as our knowledge.

3.4. Assembling mechanism

In order to investigate the mechanism of the SA process, some comparative experiments have been carried out. It is found that the absorbance of the substrate only treated by P^+ did not increase after being immersed in PAN solution and rinsed by DMF, indicating that the positively charged surface has very poor ability to absorb PAN from its solution and the acid of the surface is essential to the absorption process. We may conclude that the acid–base reaction of carboxylic acid with amine and imine groups in PAN is the driving force for the process.

As for PAA/$(NH_4)_2S_2O_8$ system, the immersing of PAN base film obtained in step(1) into PAA solutions is important for the subsequent adsorption of another monolayer of PAN. If PAN base film was only treated with $(NH_4)_2S_2O_8$ solution, another monolayer of PAN cannot be assembled onto the surface in the following step. However, the process can be continued if PAA was included in $(NH_4)_2S_2O_8$ solution or the film was subsequently treated by PAA solution. It is implied that the PAA has been absorbed onto the PAN film. We inferred that the acid–base reaction between PAN and PAA has taken place, although PAN cannot be doped by PAA in the presence of $(NH_4)_2S_2O_8$. The acid–base reaction still drove the assembling process in the PAA/$(NH_4)_2S_2O_8$ system.

The as-assembled film has good adhesion to the substrate. The PAN film prepared by the casting method can be peeled off by immersing the film in water for several minutes [16]. However, the film fabricated by the SA technique can

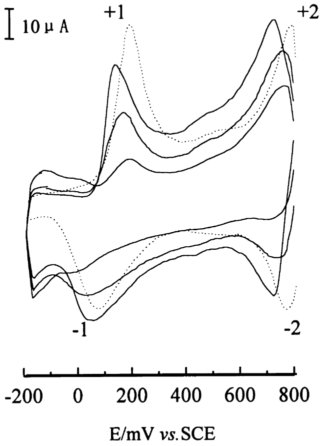

Fig. 6. Cyclic voltammograms of the self-assembled PAN/PAA films with 3, 6, 9 bilayers, respectively, in 0.5 M H_2SO_4 at 50 m VS^{-1}. 0.2% PAN was used for assembling.

adhere so strongly to the substrate that it can resist thorough rinsing by water and DMF. The strong adhesion results from the chemical bonding between the film and the surface of the substrate. In addition, the polymeric acid, PAA, does not only play a role as a dopant to PAN, but also as a “glue” between PAN layers to make the film very solid. Good adhesion is very advantageous to applications in electronic devices.

3.5. Electrical and electrochemical properties

The electrical conductivity of the self-assembled film with eight PAN/PAA layers is 0.05∼1 S cm^{-1} for ammonium persulfate free system by four-probe method. It is sensitive to humidity and NH_3 and may find applications in chemical sensors [17]. However, the conductivity of PAN/PAA($(NH_4)_2S_2O_8$) films is less than 10^{-6} S cm^{-1}.

Like PAN films prepared by other methods, the films fabricated by the SA technique may be used for electrochromic devices. Fig. 5 shows the visible spectra of the films assembled on ITO glass at various potentials.

Stepp et al. has fabricated electrochromic viologen polyelectrolyte multilayers by layer-by-layer SA method [18]. Our method is compatible with theirs as PAA may act as a polyanion and can absorb vilogen cation via electrostatic interaction. That is to say, many other electrochromic materials can be fabricated into a film by SA method and the thickness of each layer can be manipulated at nanometer scale. If the materials are appropriately chosen, the electrochromic devices with all-color display may be fabricated by this technique.

Table 1
Potentials at current peaks of PAN/PAA with different layers

Potential (*V*)	E_{p+1}	E_{p-1}	E_{p+2}	E_{p-2}
$(PAN/PAA)_3$	0.19	−0.02	0.76	0.71
$(PAN/PAA)_6$	0.17	0.04	0.76	0.74
$(PAN/PAA)_9$	0.14	0.06	0.72	0.72
$(PAN)_{EP}$[a]	0.19	0.07	0.79	0.76

[a] $(PAN)_{EP}$: PAN film prepared by electropolymerization.

The cyclic voltammograms (CVs) of PAN/PAA films with 3, 6, 9 bilayers in 0.5 M H_2SO_4 solution were shown in Fig. 6. The CV curve of PAN film prepared by the electropolymerization of 0.1 M aniline in 0.5 M H_2SO_4 was also shown in the figure for comparison. These CVs are similar but with some differences. The potentials at current peaks are shown in Table 1. The first oxidation peak (E_{p+1}) shifted to lower potentials with the increase of the thickness of the films. However, the corresponding reduction peaks (E_{p-1}) shifted to higher potentials with the increase of the thickness. We cannot explain this phenomenon so far. As for the second oxidation/reduction peaks, the peaks both shifted to the lower potentials with the increase of the thickness. We think that the PAA in the films may account for this change. PAA is a weak acid and it would hinder the diffusion of H^+ into the films. The apparent pH inside the films is higher than that in the solution. The thicker PAN/PAA film is, the more obvious the effect is. It has reported that the second peaks are pH dependent and the peaks shift negatively with the increase of pH [19]. The apparent pH increased with more number of PAN/PAA layers assembled onto the film and led to the shift of the second peaks to lower potentials. Further study is in progress to investigate the electrochemical properties of various self-assembled PAN films.

4. Conclusion

The ultrathin films of PAN/PAA were fabricated by layer-by-layer SA technique based on the acid–base reaction between PAN and PAA. The thickness of the films can be controlled at nanometer scale by solution chemistry and assembling times. The oxidation states of PAN can also be manipulated by solution chemistry. The films may be used for electrochromic devices. It is found that the PAA and the thickness of films may affect the electrochemical properties of PAN films.

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References

[1] MacDiarmid AG, Chiang JC, Richter AF, Epstein AJ. Synth Met 1987;18:285–290.
[2] Agbor NE, Petty MC, Monkman AP. Sensors and Actuators B 1995;28:173–179.

[3] Dong SJ, Che GL, Xie YW. Chemically modified electrodes. 1st ed. Beijing: Chinese Science Press, 1995. p. 338–350.

[4] Ho PKH, Granstrom M, Friend RH, et al. Adv Mater 1998;10(10):769–774.

[5] Paloheimo J, Laakso K, Isotalo H, Stubb H. Synth Met 1995;68:249–257.

[6] Dhanabalan A, Dabke RB, Datta SN, Kumar NP, Major SS, Talwar SS, Contractor AQ. Thin Solid Films 1997;295:255–259.

[7] Fuzzy DG. Science 1997;277:1232–1237 and references therein.

[8] Decher G, Hong JD, Schmitt J. Thin Solid Films 1992;210–211:831–835.

[9] Cheung JH, Stockton WB, Rubner MF. Macromolecules 1997;30(9):2712–2716.

[10] Stockton WB, Rubner MF. Macromolecules 1997;30(9):2712–2716.

[11] Liao YH, Levon K. Polym Mater Sci Engng 1993;69:327–328.

[12] Li D, et al. Thin Solid Films 1999;1.

[13] Cao Y, Andreatta A, Heeger AJ, et al. Polymer 1989;30:2305–2311.

[14] Kotov NA, Dekany I, Fendler JH. J Phys Chem 1995;99:13065–13069.

[15] Kang ET, Neoh KG, Tan KL. Prog Polym Sci 1998;23:277–324.

[16] Angelopoulos M, Asturias GE, Ermer SP, et al. Mol Cryst Liq Cryst 1988;160:151–163.

[17] Li D et al., in preparation.

[18] Stepp J Schlenoff. J Electrochem Soc 1997;144(6):L155–L157.

[19] Cai LT, Chen HY. J Appl Electrochem 1998;28:161–166.