DAR Assisted Layer-by-Layer Assembly of Aromatic Compounds

JIANG, Si-Guang(姜思光) CHEN, Xiao-Dong(陈晓东) ZHANG, Li(张莉) LIU, Ming-Hua* (刘鸣华)
Key Laboratory of Colloid and Interface Science, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

A facile DAR (diphenylamine-4-diazonium-formaldehyde resin) assisted layer-by-layer (LbL) assembly of ultrathin organic film of aromatic compounds has been investigated. The multilayer of pyrene or anthracene was fabricated through simple dipping of the glass slide into the mixed solution of DAR with the target compounds. In this method, DAR acted as an assistant compound to help the assembling of the aromatic compounds. Such a convenient deposition method not only reserves the advantages of the traditional LbL technique but also simplifies the technique and extends the effectiveness of LbL technique to small molecules without any charge.

Keyword DAR, layer-by-layer, pyrene, anthracene

Introduction

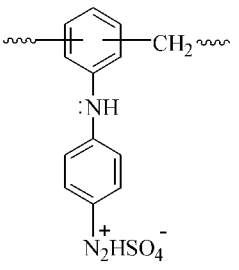
Many functional organic and/or inorganic building blocks are assembled into ultrathin molecular films[1-5], which have potential applications in composites, catalysis, microelectronics, nonlinear optics, sensors and display fields.[6-9] A number of ways such as Langmuir-Blodgett (LB) technique,[10,11] self-assembly monolayer (SAM) method[12-15] and layer-by-layer (LbL) deposition[16] are used to prepare the ultrathin multilayer films. All of these techniques basically require that the film-forming molecules have some specific structural features. For example, amphiphiles are usually suitable for the fabrication of Langmuir-Blodgett films. While those compounds containing-SH group are appropriate for the SAM on gold surface. For LbL method, molecules with complementary properties such as hydrogen bonding and electrostatic interactions are favored. For those simple aromatic compounds such as pyrene and anthracene, none of the above method is suitable for the deposition. DAR (diphenylamine-4-diazonium-formaldehyde resin) has been attracting much interest as a component to assemble various LbL ultrathin films since the pioneer work of Zhang and Cao 's groups.[17] In following their work, we have found that simply dipping of the glass slide into a mixed solution of DAR with the target compounds pyrene or anthracene can produce the ultrathin films containing them. This dipping process can be repeated many times and an ultrathin multilayer is efficiently deposited layer-by-layer. DAR assisted LbL deposition not only reserves the advantages of LbL "beaker technique"[16] but also controls the thickness of ultrathin film in a nanoscale.

Experimental

Materials and Instruments

DAR, as shown in Scheme 1, was synthesized according to a reported method.[18] The starting compound 4-diazodiphenylamine sulfate and paraformaldehyde were purchased from Tokyo Kasei. Aromatic compounds pyrene and anthracene were recrystallized before use. Quartz plate was treated with "piranha solution" [a 30∶70 mixture of 30% hydrogen peroxide (H_2O_2) and concentrated sulfuric acid (H_2SO_4)] at 80 ℃ for 1 h, followed by thoroughly rinsing with Milli-Q water. A JASCO V-530 spectrophotometer was used for the UV-vis absorption measurements of the multilayer films, and a JASCO FT/IR-660 Plus was used for the IR measurements. Atomic force microscopy (AFM) (Nanoscope III A, Digital Instruments) was utilized to visualize the surface morphology of the films. Steady-state fluorescence spectra were recorded using an F-4500 spectrofluorometer at room temperature. In photoirradiation experiment, a UV light (254 nm, 20 W) was used.

Scheme 1 Molecular structure of DAR.



* E-mail: liumh@iccas.ac.cn; Fax: 010-62569564; Tel.: 010-62569563
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Fabrication of multilayer

The following solutions were used to prepare DAR or DAR assisted aromatic compounds multilayer films: a clean quartz plate was immersed in aqueous solutions of DAR (7 mg/mL) or the mixture of DAR and the aromatic compounds solution (1 mg/mL). In the case of mixed solution of DAR with aromatic compounds, 75 volume% of acetone was used in order to dissolve the organic compound. After immersing for 5 min, the plate was pulled out from the solution and washed with Milli-Q water and dried in air. Repeating the above steps can afford the formation of the multilayer films. All the experiments were performed in dark.

Results and discussion

DAR has been used as a polycation to fabricate ultrathin films by LbL and the stability of the formed ultrathin film is increased by photoirradiation.[19-22] We have reported that DAR itself can form ultrathin film through consecutive deposition from aqueous DAR solution.[23] It was found that by simply dipping the quartz plate into the aqueous solution of DAR, a DAR film could be uniformly deposited layer-by-layer. More interestingly, we have found that small molecules can be co-deposited layer-by-layer to form a uniform ultrathin film by mixing them with DAR.[23] Here, we show further examples of the successful deposition of pyrene and anthracene. These aromatic compounds cannot be assembled into ultrathin films using traditional LbL method because they have neither any charges nor functional groups. However, upon mixing with DAR, an ultrathin multilayer film containing them can be fabricated through the deposition method. Fig. 1 shows the UV-vis spectra of the deposited films as a function of deposition cycle. Characteristic absorption of the pyrene is observed at 243, 266, 276, 327 and 343 nm, and the absorption at 383 nm ascribed to DAR is also seen clearly.[16,19-22,24] The intensities of these peak maxima increased linearly with the deposition cycle, indicating the uniform deposition of the two components in the film. From the comparison of the characteristic peaks of pyrene in film with those in ethanol solution (Fig. 1, dashed line), it is observed that peak maxima of pyrene are red shifted about 10 nm, which can be explained by a J-like aggregation or the ordered π-π stacking of pyrene ring in the film.

Pyrene assembled into the multilayer film showed strong fluorescence, as shown in Fig. 2. With the 340 nm excitation, the DAR-pyrene film shows emission bands at 375, 386, 395 and 470 nm. The bands at 375, 386 and 395 nm can be assigned to the monomer emission of pyrene, while the emission band at 470 nm can be assigned to the excimer band of pyrene. In addition, by changing the mixing ratio of pyrene to DAR in the solution, the amount of the aromatic compounds incorporated into each layer can be changed. They will affect the fluorescence properties of the multilayer film. From Fig. 2, it is clear that when the pyrene ratio was decreased, only monomer emission was observed. This indicated that the emission of the film can be regulated through changing the mixing ratio of pyrene to DAR.

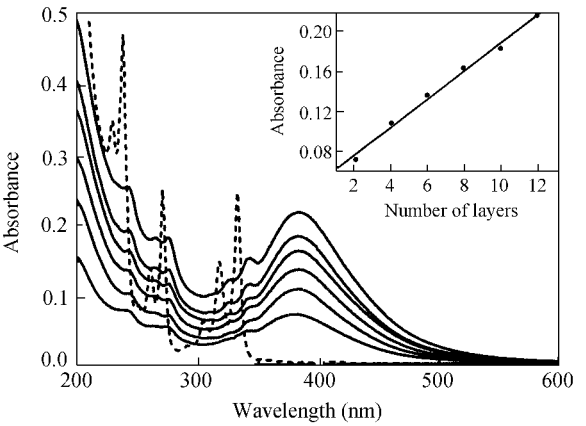


Fig. 1 UV-vis absorption spectra of DAR-pyrene multilayer film fabricated on a quartz plate using the layer-by-layer deposition (solid line) and pyrene in ethanol solution (dashed line). The insert shows the increase of absorbance at 389 nm as a function of deposition cycles.

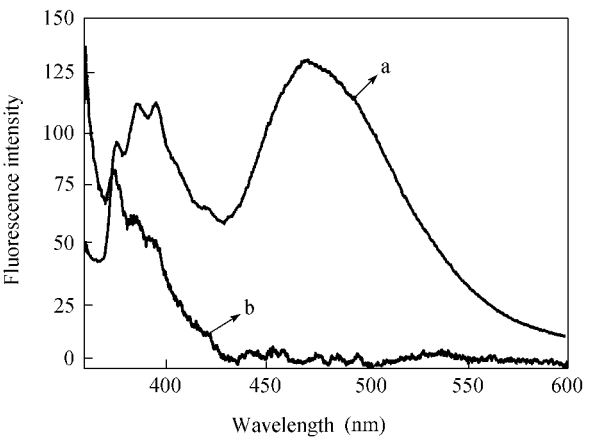


Fig. 2 Fluorescence spectra of DAR-pyrene film assembled from the solution with different DAR/pyrene ratios: (a) 1/10 and (b) 1/5. Excitation at 340 nm.

In order to make it clear whether pyrene is attached to the DAR through covalent bond prior to the consecutive deposition, we have checked the FT-IR spectra of the freshly deposited film from the DAR-pyrene solution. It has been confirmed that the characteristic bands of the diazonium group (2224 and 2171 cm^{-1}) appeared immediately after deposition. Upon photoirradiation, these vibrations disappeared.[25] This indicates that there is no reaction between DAR and pyrene in solution and pyrene was deposited through the molecular interaction between the pyrene and DAR.

Fig. 3 shows the atomic force microscopy (AFM) of one layer DAR and DAR-pyrene film on a mica surface. Smooth films are formed in both cases, a mean roughness

of 0.160 and 0.089 nm was detected for DAR and DAR-pyrene film, respectively. Many tiny pinholes are observed in DAR film, but disappeared in the DAR-pyrene film. The AFM picture indicates that pyrene and DAR are mixed uniformly in the deposited film. On the other hand, by scratching the film of DAR-pyrene, the height of the film was found to be 2.0 nm. Previously we have reported that DAR film was 1.8 nm in thickness.[23] This further suggested that pyrene and DAR are co-absorbed together in the same layer and the assemble process could be expressed in Scheme 2.

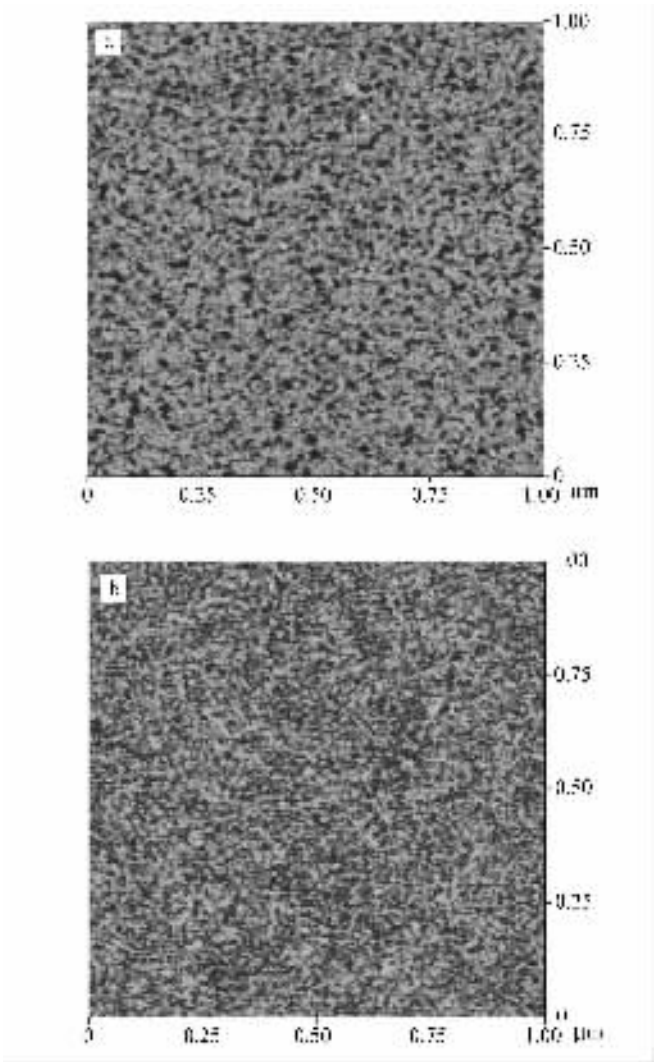
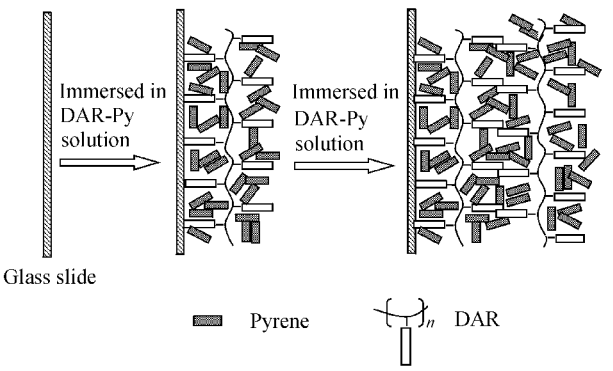


Fig. 3 AFM images of one layer of DAR (A) and DAR-pyrene (B) film on mica.

Since both the pyrene and DAR have a good delocalized π conjugate system, it is suggested that the π-π stacking between DAR and pyrene causes the successful deposition of pyrene through the assistance of DAR. Similar to the case of pyrene, anthracene can also be uniformly assembled into a multilayer film through the assistance of DAR, as shown in Fig. 4. In order to further support this, we have tried other aromatic compounds. We have proved that anthracene derivative such as 9-hydroxymethylanthracene can easily be assembled into the film, but naphthalene could not be deposited. This can be explained by the relatively weaker interaction between the naphthalene ring and the aromatic rings in DAR than those with large conjugate systems.

Scheme 2 Schematic representation of the assemble process of DAR-pyrene multilayer film.



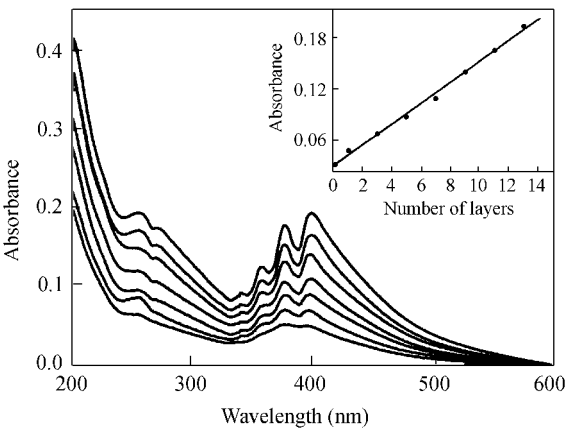


Fig. 4 UV-vis absorption spectra of DAR-anthracene multilayer film fabricated on a quartz plate using the layer-by-layer deposition. The insert shows the increase of absorbance at 389 nm as a function of deposition cycles.

Conclusions

We have successfully fabricated the ultrathin films of some aromatic compounds without any charge by a DAR assisted LbL method. This technique provides a facile way to assemble ultrathin films of small molecules either from aqueous or from organic solution. This method shows that very weak force such as π-π stacking might also become the driving force in fabricating film. The method is not only simple (only deposition from one solution, no need for alternative deposition from different solutions) but also applicable to small aromatic compounds without any charges.

References

1 Ostrander, J. W.; Mamedov, A. A.; Kotov, N. A. *J. Am. Chem. Soc.* **2001**, *123*, 1101.

2 Cassagneau, T.; Fendler, J. H. *J. Phys. Chem. B* **1999**, *103*, 1789.

3 Rogach, A. L.; Koktysh, D. S.; Harrison, M.; Kotov, N. A. *Chem. Mater.* **2000**, *12*, 1526.

4 Kometani, N.; Nakajima, H.; Asami, K.; Yonezawa, Y.; Kajimoto, O. *J. Phys. Chem. B* **2000**, *104*, 9630.

5 He, J.; Bian, S.; Li, L.; Kumar, J.; Tripathy, S. K. *J. Phys. Chem. B* **2000**, *104*, 10513.

6 Klein, D. L.; Roth, R.; Lim, A. K. L.; Alivisatos, A. P.; McEuen, P. L. *Nature* **1997**, *389*, 699.

7 Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226.

8 Li, D.; Ratner, M. A.; Marks, T. J.; Zhang, C. H.; Yang, J.; Wong, G. K. *J. Am. Chem. Soc.* **1990**, *112*, 7389.

9 Lee, S.; Balasubramanian, S.; Kim, D. Y.; Viswanathan, N. K.; Bian, S.; Kumar, J.; Tripathy, S. K. *Macromolecules* **2000**, *33*, 6534.

10 Ulman, A. *An Introduction to Ultrathin Organic Films, From Langmuir to Self-Assembly*, Academic Press, Inc., San Diego, CA, **1991**.

11 Roberts, G. G. *Langmuir-Blodgett Films*, Plenum Press, New York and London, **1990**.

12 Sellers, H.; Uleman, A.; Shnidman, Y.; Eilers, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 9389.

13 McGovern, M. E.; Kallury, K. M. R.; Thompson, M. *Langmuir* **1994**, *10*, 3607.

14 Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358.

15 Whitesides, G. M.; Laibins, P. E. *Langmuir* **1990**, *6*, 87.

16 Decher, G. *Science* **1997**, *277*, 123.

17 Sun, J.; Wu, T.; Sun, Y.; Wang, Z.; Zhang, X.; Shen, J.; Cao, W. *Chem. Commun.* **1998**, 1853.

18 Cao, W.; Ye, S.; Cao, S.; Zhao, C. *Macromol. Rapid Commun.* **1997**, *18*, 983.

19 Sun, J.; Wang, Z.; Sun, Y.; Zhang, X.; Shen, J. *Chem. Commun.* **1999**, 693.

20 Zhong, H.; Wang, J.; Jia, X.; Li, Y.; Qin, Y.; Chen, J.; Zhao, X.; Cao, W.; Li, M.; Wei, Y. *Macromol. Rapid Commun.* **2001**, *22*, 583.

21 Sun, J.; Wu, T.; Liu, F.; Wang, Z.; Zhang, X.; Shen, J. *Langmuir* **2000**, *16*, 4620.

22 Cao, T.; Wei, L.; Yang, S.; Zhang, M.; Huang, C.; Cao, W. *Langmuir* **2002**, *18*, 750.

23 Jiang, S.; Chen, X.; Zhang, L.; Liu, M. *Thin Solid Films* **2003**, *425*, 117.

24 Tedeschi, C.; Caruso, F.; Mohwald, H.; Kirstein, S. *J. Am. Chem. Soc.* **2000**, *122*, 5841.

25 Chen, J.; Luo, G.; Cao, W. *Macromol. Rapid Commun.* **2001**, *22*, 311.

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