

Note

FABRICATION OF SELF-ASSEMBLY DNA-C₆₀ MULTILAYER FILMS*

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Abstract Electrostatic layer-by-layer self-assembly multilayer films were successfully fabricated from C₆₀-ethylenediamine adduct (C₆₀-EDA) and DNA. Under visible light irradiation, DNA is ready to be cleaved and the films are destroyed.

Key words Self-assembly, Photo-induced cleavage, DNA, C₆₀

INTRODUCTION

Electrostatic layer-by-layer self-assembly (ESA) ultrathin films have attracted considerable interest since they were first introduced in 1992^[1, 2]. The deposition mechanism and film structure have been studied extensively, while the resulting films find potential application in a variety of fields, one of which is to perform chemical reactions in the films. Light or heat-induced reactions were often used to improve the film stability^[3, 4]. Under certain conditions, however, the decomposition of film may also be interesting. Up to now, studies on this topic are rather limited^[5]. The cleavage of DNA is an important process and photo-induced DNA cleavage in solution has been studied extensively^[6, 7]. In order to investigate this reaction in a solid film, we fabricated the ESA film from DNA and C₆₀-ethylenediamine adduct (C₆₀-EDA).

EXPERIMENTAL

C₆₀-EDA was synthesized according to Ref. [8]. Elementol analysis corresponds to C₆₀(NH₂CH₂CH₂NH₂)₄ (C: 57.93, N: 8.38, and H: 3.44). Its chloride was obtained by reaction with HCl. Polyacrylic acid (PAA) was prepared at 70°C by free radical polymerization of acrylic acid in water using isopropyl alcohol as chain transfer agent and potassium persulfate as initiator. Ionene 6,6 was synthesized via the successive Menschutkin reaction of diamine and dibromide in DMF according to Ref. [9].

Quartz slides were used as substrate. After being treated in H₂SO₄/H₂O₂ mixture (7:3 V/V), the slide was first immersed in a cationic solution (C₆₀-EDA or ionene 6,6) for 4 min. After washing with water thoroughly, it was air-dried. Then the slide was immersed in an anionic solution (DNA or PAA) for another 4 min, washed with water thoroughly and air-dried. Films were fabricated by repeating this alternate deposition process.

To investigate the photoreaction, the film was immersed in water and then it was irradiated under visible light with an irradiation intensity of 0.8 mW/cm². UV-vis spectra of the film were measured at an interval of 30 min. In order to keep the temperature constant, a double wall reaction cell with a thermostat was used. The

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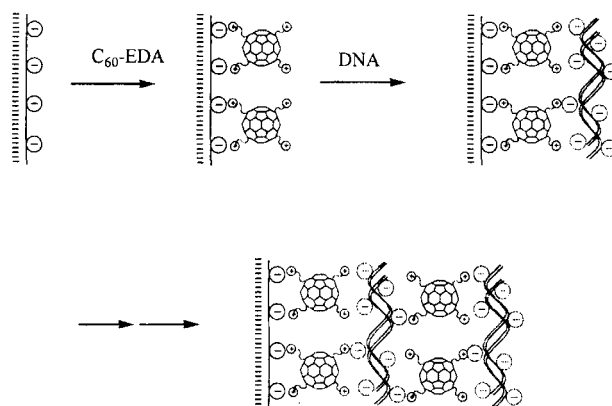
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temperature of the system was maintained at 25°C.

RESULT AND DISCUSSION

The self-assembly of C₆₀-EDA and DNA is schematically shown in Scheme 1. The self-assembly process was monitored using the UV-vis spectrum. As shown in Fig. 1, the absorbance intensity of the film increases with increasing number of dipping cycles. The peaks at 195 nm and 268 nm are attributed to the absorption of C₆₀-EDA and DNA, respectively, which indicates both C₆₀-EDA and DNA are assembled into the film successfully. The absorbance at both 195 nm and 268 nm increases linearly with the number of dipping cycles, indicating the film was fabricated uniformly.



Scheme 1 Fabrication of self-assembly films from C₆₀-EDA and DNA

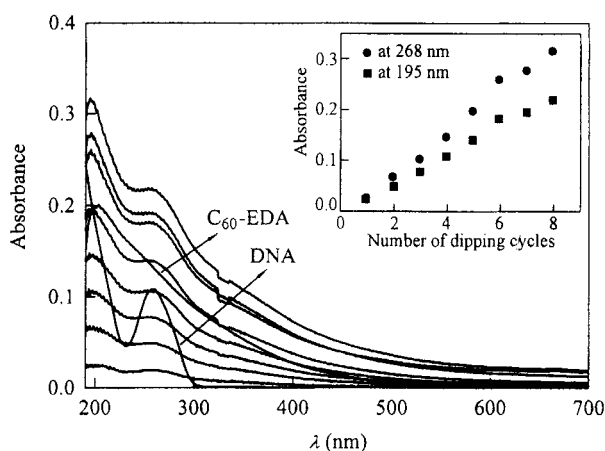


Fig. 1 The UV-vis spectra of the self-assembly film from C₆₀-EDA and DNA with various dipping cycles
Number of dipping cycles (from bottom to top): 1–8

The morphology of an 8-bilayer film fabricated on a silicon slide was studied by AFM. The image is shown in Fig. 2. The film exhibits a dome-like structure with a diameter of about 25 nm. The average roughness is calculated to be 5.1 nm, indicating that the film is relatively smooth.

Under light irradiation, DNA is cleaved readily by C₆₀-EDA. The UV-vis absorption intensity of the (DNA-C₆₀-EDA)₁₀ film drops under light irradiation (Fig. 3). After irradiation for 3.5 h, the absorbance of the film at 268 nm decreases by 50.5%. As a control, we measured the absorption spectra of another film that was immersed in water in darkness. No significant change was observed (Fig. 4). The result indicates that cleavage of DNA is

induced by light irradiation. In contrast, the absorbance of an (ionene 6,6-DNA) $_{10}$ film remains unchanged under light irradiation, indicating C_{60} -EDA acts as the sensitizer in the reaction.

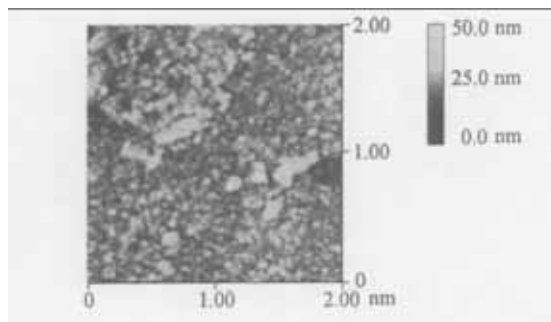


Fig. 2 AFM image of an 8-bilayer film fabricated on silicon slide

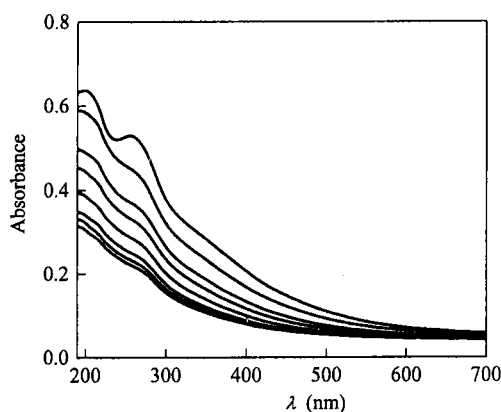


Fig. 3 UV-vis spectra of the (DNA- C_{60} -EDA) $_{10}$ film after exposing to visible light for various time
Irradiation time (from top to bottom): 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 h

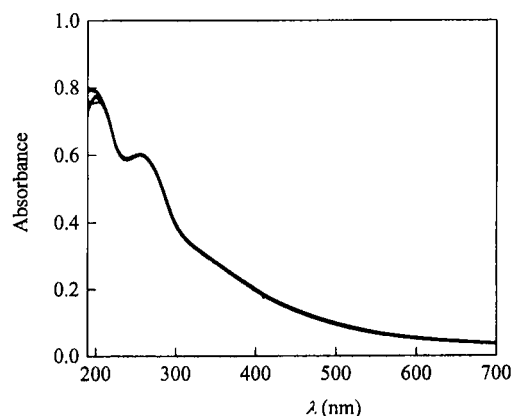


Fig. 4 UV-vis spectra of the (DNA- C_{60} -EDA) $_{10}$ film immersed in water in darkness
Immersion time: 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 h

This initial result indicates that photo-induced cleavage of DNA by C_{60} -EDA can take place in the self-assembly film. The effect of the film structure on the reaction and the reaction mechanism are now under active investigation.

REFERENCES

- 1 Decher, G., Hong, J.D. and Schmitt, J., *Thin Solid Films*, 1992, 210: 831
- 2 Decher, G., *Science*, 1997, 277: 1232
- 3 Chen, J., Huang, L., Ying, L., Luo, G., Zhao, X. and Cao, W.X., *Langmuir*, 1999, 15: 7208
- 4 Harris, J.J., DeRose, P.M. and Bruening, M.L., *J. Am. Chem. Soc.*, 1999, 121: 1978
- 5 Bertrand, P., Jonas, A., Laschewsky, A. and Lagras, R., *Macromol. Rapid Commun.*, 2000, 21: 319
- 6 An, Y.Z., Chen, C.H.B., Anderson, J.L., Sigma, D.S., Foote, C.S. and Rubin, Y., *Tetrahedron*, 1996, 52: 5179
- 7 Higashi, N., Inoue, T. and Niwa, M., *Chem. Commun.*, 1997: 1507
- 8 Chen, Y., Fang, P., Zhu, L. and Sheng, R., *Chem. J. Chin. Univ.*, 1998, 19: 1011
- 9 Rambaum, A. and Noguchi, H., *Macromolecules*, 1972, 5: 261