Cucurbit[8]uril-based stimuli-responsive films as sacrificial layer for preparation of free-standing thin films

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Introduction

Free-standing thin films have been extensively investigated for use in a wide range of applications from optics to biomedical purposes. Methods for the fabrication of free-standing thin films have attracted considerable attention.

In this work, we reported a facile supramolecular method to prepare free-standing thin films by designing a stimuli-responsive film based on CB[8] host-guest interactions as a sacrificial layer. The film was fabricated via layer-by-layer assembly of poly(acrylic acid) (PAA) and supramolecular pseudo-polycation. Owing to the CB[8] ternary complex, the film exhibited disassembly properties in response to aminoadamantane (Ad) and sodium dithionite ($Na_2S_2O_4$). Therefore, the film was capable of releasing top free-standing thin films.

Method

◆ A dextran modified with 2-naphthoxy group (NpD) was synthesized via EDC-mediated coupling method. The neutral NpD was then conversed into a pseudo-polycation MV-CB[8]-NpD through equimolar complexation with the doubly-charged binary complex of CB[8] and MV in water. The expected ternary complex formation was confirmed by ^{1}HNMR measurement and UV-via spectroscopy.

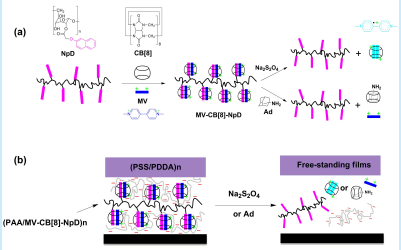

Figure 1. (a) Schematic of the modified dextran with controlled charge properties through supramolecular complexation/decomplexation (b) Schematic of the preparation of free-standing films.

◆The MV-CB[8]-NpD pseudo-polycation was then employed in spin-assisted LBL assembly with polyanion PAA. The thickness of the PAA/MV-CB[8]-NpD multilayers was followed by ellipsometry.

◆The disassembly behaviour of the PAA/MV-CB[8]-NpD multilayer films was investigated by external trigger of competitive guest Ad or reduction agent $Na_2S_2O_4$.

◆ To obtain the free-standing films, a hybrid $(PAA/MV\text{-}CB[8]\text{-}NpD)_7$-$(PSS/PDDA)_n$ film was prepared by alternating spin deposition of PSS and PDDA on top of the sacri fi cial layer of PAA/MV-CB[8]-NpD, and then immersed in 3 mg/mL $Na_2S_2O_4$ or Ad solutions.

Results

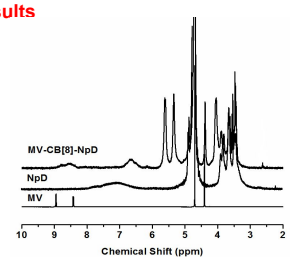

Figure 2. 1H-NMR spectra of MV, NpD and the mixture MV-CB[8]-NpD in D_2O.

◆ HNMR results confirmed the successful synthesis of NpD. the extensive broadening and upfield shift of aromatic proton signals in the ^{1}HNMR spectra suggested the formation of the CB[8] ternary complex.

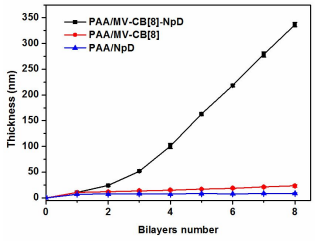

Figure 3. LBL assembly of PAA and MV-CB[8]-NpD growth followed by spectroscopic ellipsometry.

◆ A regular assembly process is observed. While the control system of PAA with MV-CB[8] or NpD shows almost no film growth, suggesting that the pseudo-polycation was indeed formed and its stable multivalent supramolecular polymer structure was suitable for electrostatic LBL assembly.

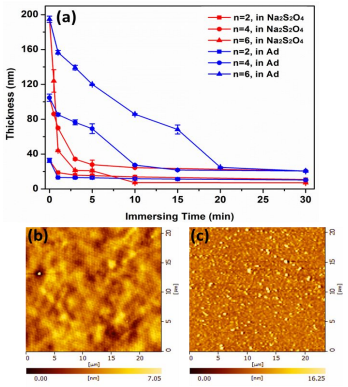

Figure 4. (a) Response of films $(PAA/MV\text{-}CB[8]\text{-}NpD)_n$ in $Na_2S_2O_4$ or Ad aqueous solutions. (b) AFM images of the sacrificial layer composed of $((PAA/MV\text{-}CB[8]\text{-}NpD)_7$ on a silicon substrate. (c) The substrate after the disassembly of the sacrificial layers through immersing in Ad solutions.

◆ Film disassembly through Ad stimuli is thickness dependent, while it is thickness independent by $Na_2S_2O_4$ stimuli.

Surface distinctly changed also suggested triggered disassembly of the multilayer films.

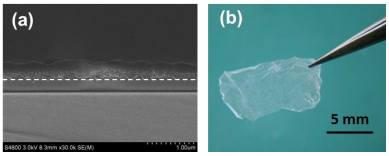

Figure 5. (a) Cross-section SEM images of a hybrid film $(PAA/MV\text{-}CB[8]\text{-}NpD)_7/(PSS/PDDA)_{40}$. (b)Photograph of a $(PSS/PDDA)_{100}$ free-standing film in air.

◆ Fig. 5a shows the cross-sectional SEM image of the hybrid film when n is 40. After several minutes of immersion in $Na_2S_2O_4$ or Ad solutions, the PSS/PDDA films released from the substrate.

Fig. 5b shows one photograph of a flat free-standing $(PSS/PDDA)_{100}$ film in air.

Conclusion

In conclusion, we developed a facile supramolecular method to prepare free-standing thin films. This method employs a sacrificial multilayer films composed of PAA and a CB[8] ternary complex modified dextran. The disassembly of the sacrificial films triggered by the disruption of the CB[8] ternary complex in the presence of competitive guest or reduction agent. These unique stimuli responsive multilayer films allows for effective triggered release of top thin films.

References

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