Spray layer-by-layer assembly based on bioinspired polydopamine-FeIII coordination bond for superhydrophobic films

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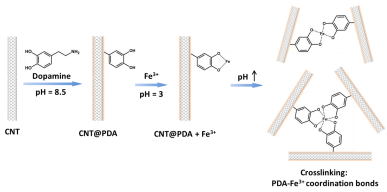
Introduction

Spray layer-by-layer (LbL) assembly technique has been developed for fabricating functional films rapidly and efficiently. While, the spraying method generally requires relatively fast interaction between the building blocks. In this study, inspired by mussel bysuss, we investigated the effect of the very fast and pH-dependent catechol-Fe^{3+} coordination bond on fabricating a composite carbon nanotube thin film, (poly(ethylenimine)/polydopamine-coated carbon-nanotubes) (PEI/CNTs@PDA) multilayer film. We also investigated the film ' s wettability before and after treating the film with a fluorosilane using a CVD method.



Scheme 1. *Schematic illustration of modification of CNTs with polydopamine and the pH-dependent catechol-Fe^{3+} coordination and its use in crosslinking of CNT@PDA.*

Method

- CNTs@PDA solution was obtained by adding CNTs (1mg/mL) and dopamine hydrochloride (0.1mg/mL) into a Tris-HCl buffer solution (10mM, pH 8.5), followed by ultrasound dispersing and wildly stirring for 48h at room temperature. $FeCl_3$ was added into the CNTs@PDA solution.
- For the (PEI/CNTs@PDA) multilayer film, the CNTs@PDA solution with Fe^{3+} ($c(Fe^{3+})$ = 0mM, 0.5mM, 1.5mM, 2.5mM, 3.5mM, 4.5mM, pH 3) and a PEI solution (2mg/mL, pH 12) were sprayed to the substrates alternately for several times.
- pH stability experiments of CNTs@PDA and CNTs@PDA+Fe^{3+} solutions were carried out to investigate the assembly pH conditions.
- The size and zeta potential of the CNTs aggregates at pH 3 and 8.5 were measured to investigate their change in size and zeta potential.
- UV-vis spectroscopy was used to characterize the pH-dependent catechol-Fe^{3+} coordination bond.
- Thicknesses of the multilayer films were measured using a spectroscopic ellipsometer.
- Surface morphology and cross-section view of the films were observed using a SEM.
- For CVD treatment, the samples were placed in a sealed chamber in the presence of 0.6 mL triethoxy(tridecafluorooctyl)silane. The sealed chamber was placed in an oven at 130°C for 2.5 h. The films were then taken out and heated at 180°C for 1.5 h to remove unreacted silane molecules.
- Contact angles and roll-off angles of water were measured on the CVD treated films.

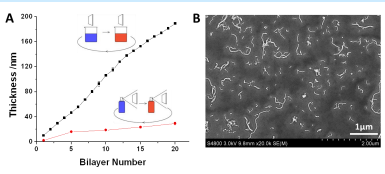


Figure 1. *(A) Thickness of dipping and spraying (PEI/CNTs@PDA) multilayer films as a function of bilayer number. (B) SEM showed sparse CNTs spreading out over the substrate after 20 cycles of spraying LbL deposition of (PEI/CNTs@PDA) film.*

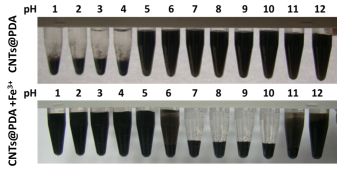


Figure 2. *Dispersion stability of CNTs@PDA solutions in the absence (up) and presence (down) of Fe^{3+} at different pH from 1 to 12.*

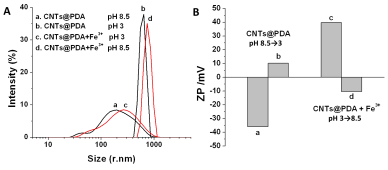


Figure 3. *Size (A) and Zeta potential (B) of the particles in solutions of CNTs@PDA without Fe^{3+} at pH 8.5 (a) and 3 (b), and with Fe^{3+} at pH 3 (c) and 8.5 (d).*

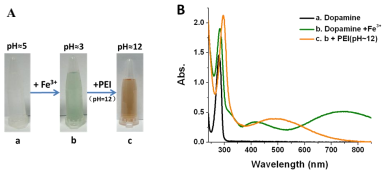


Figure 4. *Crosslinking dopamine + Fe^{3+}: (A) the color change of dopamine solution added with 0.65 mM $FeCl_3$ and a same volume of PEI (pH = 12, 2 mg/mL) solutions successively. (B) UV-Vis spectra of solution a, b and c.*

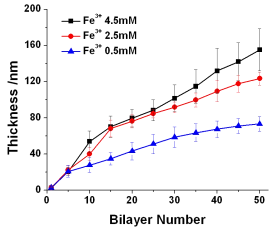


Figure 5. *The influence of the concentration of Fe^{3+} on the growth rate of the [PEI/(CNTs@PDA+Fe^{3+})] multilayer film. The concentration of Fe^{3+} increased from 0.5 mM to 4.5 mM.*

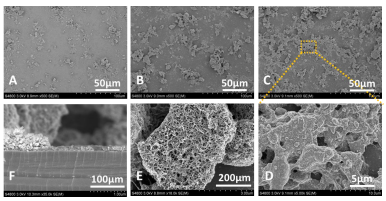


Figure 6. *SEM images of the surface morphology and cross section of [PEI/(CNTs@PDA+Fe^{3+})] multilayer films with 20 BL (A), 30 BL (B) and 50 BL (C, D, E, F, with different magnification).*

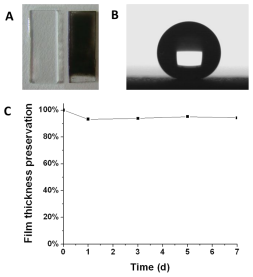


Figure 7. (A) Photographs of glass slide substrates uncovered (left) and covered with the sprayed [PEI/(CNTs@PDA+Fe^{3+})] multilayer film (right). (B) Contact angle (150.9° ± 0.3°) of the film surface. (C) Thickness of the [PEI/(CNTs@PDA+Fe^{3+})] multilayer film incubated in 150 mM EDTA for a week.

Conclusions

➢We have fabricated the [PEI/(CNTs@PDA+Fe^{3+})] multilayer film through spraying LbL assembly based on the coordination bond between CNTs@PDA and Fe^{3+}. The coordination interaction between catechol group on PDA and metal ions (Fe^{3+}) was rapidly and pH-dependent.

➢The growth of the [PEI/(CNTs@PDA+Fe^{3+})] multilayer film was Fe^{3+} concentration dependent. The thickness of the spraying LbL [PEI/(CNTs@PDA+Fe^{3+})] film was comparable with that of the (PEI/CNTs@PDA) film fabricated by dipping method. While, they showed totally different topographical features.

➢ After coated with a low surface energy silane compound, the [PEI/(CNTs@PDA+Fe^{3+})] film with hierarchical micro/nano-structures showed a superhydrophobic surface with good stabilities.

Acknowledgements

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References

1.N. Holten-Andersen, M.J. Harrington, et al. *Proc Natl Acad Sci U S A*, 2011, 108, 2651.
2.B Mizrahi, S.A. Shankarappa, et al. *Adv Funct Mater*, 2013, 23, 1527.
3.J.L. Wang, K.F. Ren,et al. *Phys Chem Chem Phys*, 2014, 16, 2936.