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Hierarchical self-assembly of dopamine into patterned structures

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Abstract: It has been demonstrated that dopamine can undergo oxidation and complicated self-reaction in aqueous solution to form so-called polydopamine (PDA). In this work, for the first time we describe the hierarchical self-assembly of dopamine into surface patterned structures. The surface fractal patterns were further created and modulated by the dynamic self-assembly of PDA nanoaggregates to develop more macroscopic ordered structure of PDA. Various surface patterns of PDA aggregates were successfully obtained by evaporative dewetting method. The effects of solution pH, type of inorganic salts and temperature on the morphology of surface pattern were investigated. The surface patterning strategy reported here is applicable to a broad range of materials, which allows the developments of materials with controllable patterned structure.

Introduction

Self-assembly process exists widely throughout nature and science. A common definition of self-assembly contains that pre-existing components, separated or distinct parts of disordered, spontaneously form ordered aggregates[1]. Coffee-ring is a well-known self-assembly process that when a drop of coffee dries on a solid surface, it leaves a ring-like deposition pattern along the perimeter. The surface patterns formed by drying liquid drops are determined by capillary flow and Marangoni flow.

The mussel-inspired dopamine (DA) chemistry has attracted much attention in recent years thanks to its potential applications in a broad range of fields. In this work, evaporation patterning of PDA aggregates was investigated under various solution and environmental conditions, which provides new insights into fundamental understanding of the interaction of PDA aggregates as well as the patterning and modification of surfaces.

Results and disscussions

Schematic illustration of self-assembly process

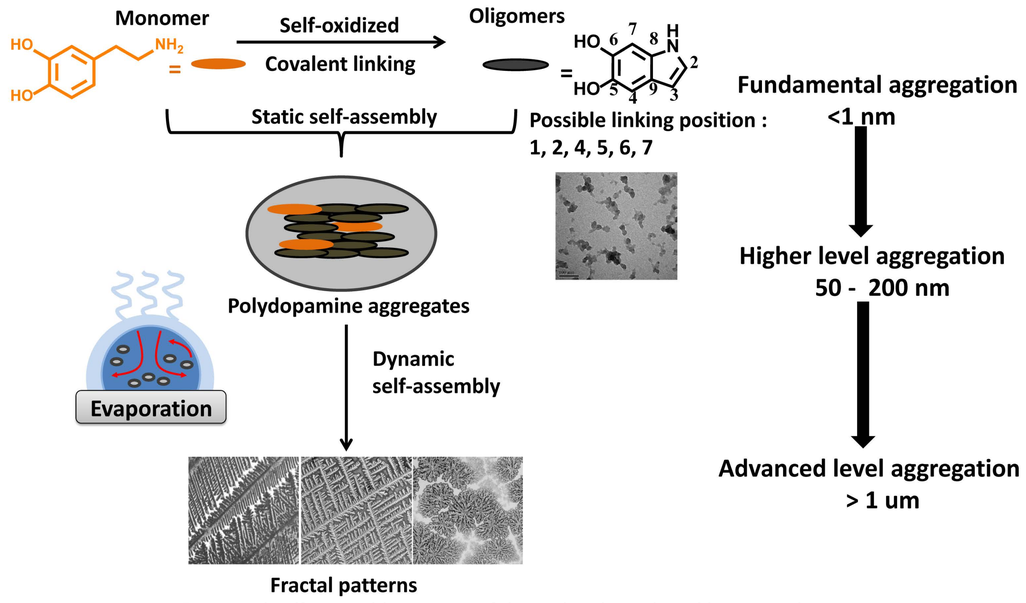

Fig. 1 Proposed self-assembly process of dopamine through multi aggregation steps

Effects of initial pH on patterns

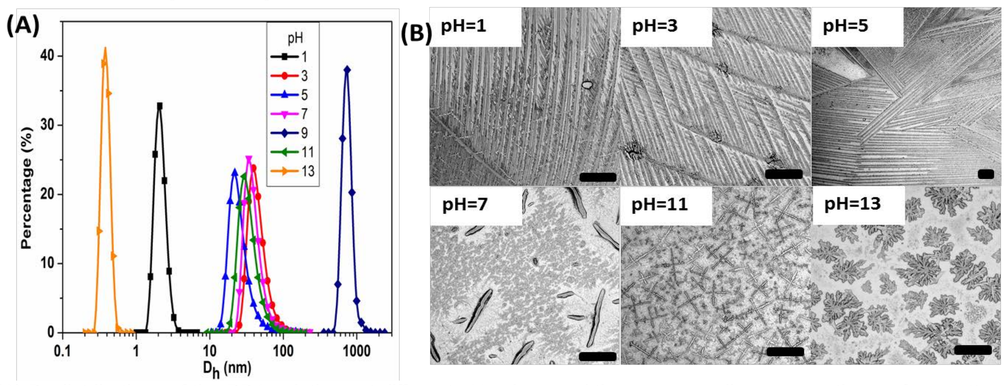

Fig.2 (A) D_h distributions of the PDA solutions at different pH values and the corresponding evaporating surface patterns on the silicon surface at 30℃ temperature (B). Scale bar is 200 um.

Characterization of the surface patterns

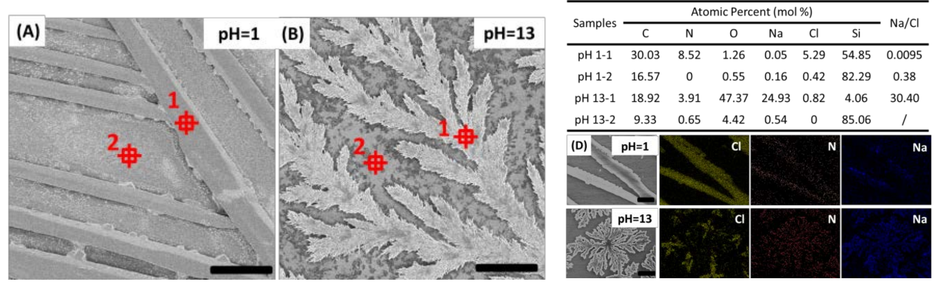

Fig. 3. SEM images of patterned surfaces prepared by (A) pH=1, (B) pH=13. The EDX results for the chosen position(C). (D) EDX mapping images of the membrane surface and distribution of Cl (yellow point), N (red point) and Na (blue point) elements on the silicon surfaces. All scale bar is 20 um.

Effects of salt concentration on surface patterns

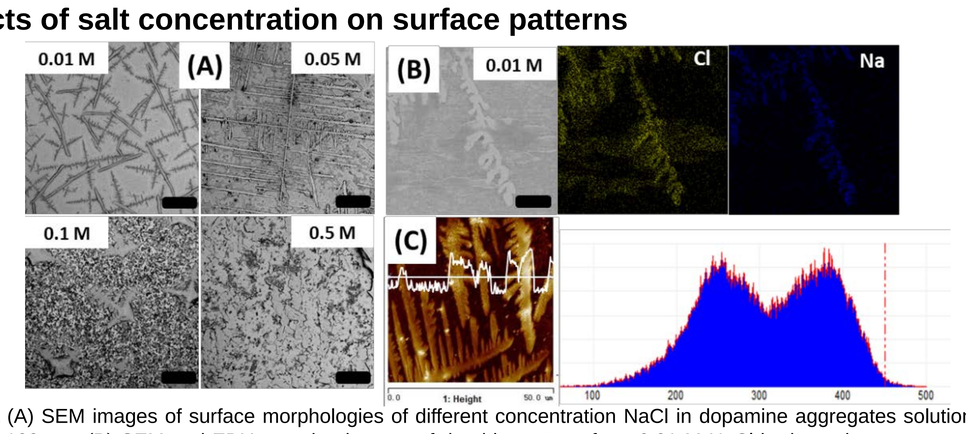

Fig. 4. (A) SEM images of surface morphologies of different concentration NaCl in dopamine aggregates solutions. Scale bar is 100 um; (B) SEM and EDX mapping images of dendrite pattern from 0.01 M NaCl in dopamine aggregate solution and distribution of Cl (yellow point), Na (blue point) element on silicon surfaces. Scale bar is 20 um here; (C) AFM images of dendrite pattern, with height profile along horizontal line is presented in it and depth distribution analysis.

Effects of different kind of salts on the morphologies

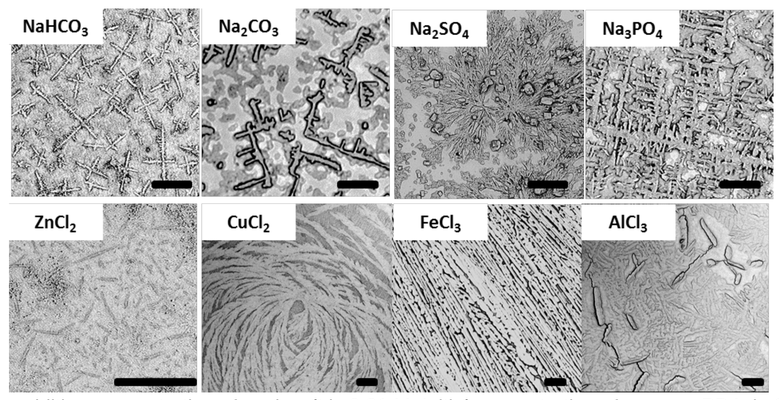

Fig. 5. The addition concentration of each salt is 0.01 M. Initial concentration of aqueousPDA is 1 g/L with pH=7 and solvent evaporation temperature is 30 ℃. The scale bar is 50 um

Proposed scheme model for pattern formation

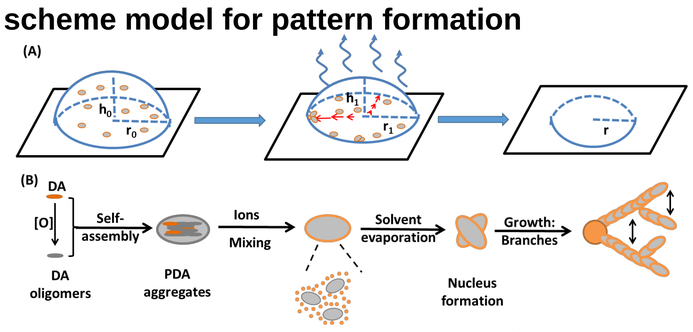

Fig. 6. (A) A scheme model for drying the aqueous solution drop. (B) A schematic illustration of PDA aggregates and their dynamic self-assembly into patterns driven by solvent evaporation.

As the evaporation process take place, PDA aggregates complex with ions diffuse by random walk and Brownian motion process in the aqueous drops. When the aggregates are pinned at the liquid-solid interface as they reach to the contact line, the aggregates form the initial nucleus. Then, newly aggregates from drop center continue to reach to the edge and adhere to the nucleus under the evaporation of water. We propose that screening effect between each branches may prevent newly aggregates to adhere until they reach to the position where this effect is too weak to screen and then form a new branch.

Conclusions

In conclusion, we investigated dynamic self-assembly of PDA aggregates induced by the solvent evaporation. After evaporative drying of these PDA with different added ions, relatively uniform patterns were formed on substrate surface, which provide a new method to construct surface morphologies. More significantly, the existing activity groups from PDA here bring a new insight in converting the patterned surface to other functional surface.

Acknowledgement

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References

[1] G. M. W. a. B. Grzybowski, *Science* **2002**, 295, 2418
[2] P. Zhang, A. Tang, B. Zhu, L. Zhu, H. Zeng, Adv. Mater. Interfaces 2017, published online.