

첨가물이 자연적 성장을 이용한 나노구조제어에 미치는 영향

서임선, 양희택, 정부기, 정성기, 조규진

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Effect of Additives for the Formation of Polypyrrole Nanopatterns Using Self-Controlled Growth

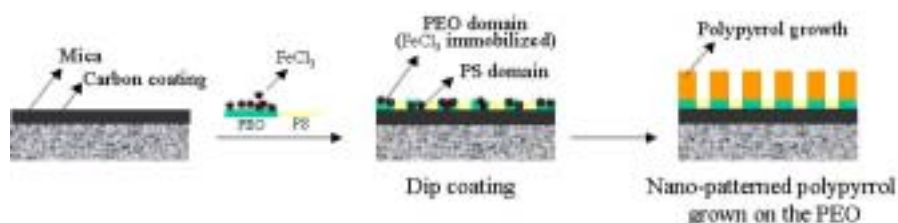
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Introduction

Conducting polymers are being used to replace both conventional metals and inorganic materials in a variety applications, especially in microelectronic devices.¹ To be effectively applied in microelectronic devices, the conducting polymers must be easily fabricated into micro- to nanoscale patterns. However, the construction of conducting polymer based microelectronic devices has been impeded by the technical challenges, mainly due to the intractability of conducting polymers.² Although it has been claimed that processibility of conducting polymers can be improved by using novel monomers, judiciously chosen dopants, and colloid systems,^{3,4} the selective deposition of conducting polymers in micro- to nanometer scales is still far from being satisfactory.

As an obvious extension of the bottom-up method, we have shown a new way for the production of 3-dimensional structures of polypyrrole (Ppy) at the nanometer scale.⁵ Our method mimics natural systems in which structurally organized organic surfaces catalytically or epitaxially induce the regioselective nucleation and growth of specifically oriented inorganic and organic structures. The process used involves the selective immobilization of FeCl_3 onto one domain of a block copolymer and the subsequent controlled release of FeCl_3 for the regioselective nucleation and growth of Ppy (Scheme 1). Although this approach can provide a simple way for the construction of pillared nanostructures of Ppy, the maximum ratio (H/D) between the diameter (D) and the height (H) of the grown Ppy was 0.1.



Scheme 1. Descriptive illustration for the growth of polypyrrole nanostructures.

Here, we further refine our approach to control the direction of Ppy growth to attain the higher H/D ratio. Our approach is quite simple. As growth rates and directions of materials in nature can be self-controlled through the response to the change of environments⁶, we would like to show that how the growth direction of the regioselectively nucleated Ppy can be self-controlled to the direction of surface normal. In this report, the results for how the direction of Ppy growth can be self-controlled by adding additives into the standard reaction medium will be reported.

Experimentals

To form a template, 0.1 mg of polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) (Mn 58600-*block*-31000, with 1.03 polydispersity) was dissolved in 11 mL of a mixed solvent of chloroform and acetonitrile with a volume ratio of 10:1. 0.03 mg of FeCl₃ was then added to the block copolymer solution, and a thin film was prepared by dipping of the substrate (carbon-coated mica) in the solution. After annealing the film at 150 °C under an inert atmosphere, the solvent evaporated, and an ordered monolayer of PS-*b*-PEO "precipitated" onto the surface and collapsed. Noncontact AFM (Park Scientific Autoprobe CP) with silicon cantilevers (ultralevers, 2 m thick, resonant frequency *ca.* 320 kHz; Park Scientific) has been used to attain the topological images of the resulting pattern. The immobilized FeCl₃ can be slowly released by dipping the film into a selected medium. For example, using diethyl ether as a standard medium, FeCl₃ can be released due to the swelling of the PEO units in the medium.

For the formation of nano-structured Ppy, 1 mM pyrrole in diethyl ether was used. To study the influence of additives for the growth orientation of Ppy, various amounts of surfactant and silicon oil were added into the medium. The film containing immobilized FeCl₃ was dipped into the pyrrole solution for 2 to 12 h. After gently removing the film from the solution, it was washed with diethyl ether and dried under vacuum at room temperature for 24 h. The dried film was characterized using AFM with the noncontact mode.

Results and Discussion

The topological AFM images of microphase-separated PS-*b*-PEO films was observed as protrusions (bright spots in the AFM image of Fig. 1a). Similar structures are found in a certain concentration range for amphiphilic diblock copolymers. Fig. 1b shows the spinodal structures with a typical height of about 2 nm and a mean diameter of about 110 nm. FeCl₃ is selectively solubilized preferentially in the PEO domain (bright spots in the AFM image of Fig. 1a) of the block copolymer, where it is coordinated and stabilized by the ether units. In other words, the trigger in the thin film is exclusively immobilized in the spinodal structures of PEO. The regioselective immobilization of FeCl₃ was proved using TEM. Since the TEM image was taken without any staining, the PS-*b*-PEO film is not visible because of its small electron density. However, the immobilized FeCl₃ was observed as dark spots (Fig. 1c), and this was verified by energy-dispersive X-ray (EDX) analysis of the elements present. The sizes of the dark regions (Fig. 1c) are almost the same as the sizes of the protrusions in Fig. 1.

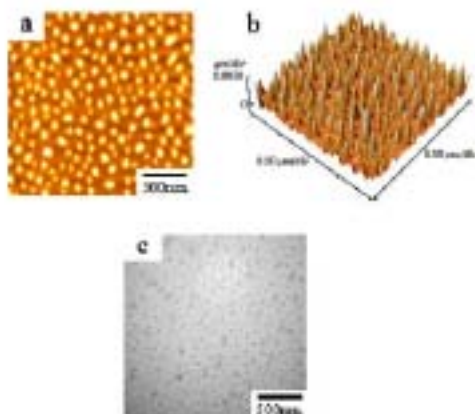


Figure 1. (a) Topological AFM image, (b) 3-dimensional AFM image, and (c) TEM image of the trigger-immobilized nano-structures formed by PS-*b*-PEO deposited on a carbon-coated mica substrate.

Fig. 2a and 2b show the AFM images obtained for a sample with a polymerization time of 2 h. The protruded surface structures in Fig. 2c have heights of 10 nm and diameters of 110 nm, compared with heights of 2 nm and diameters of 110 nm for the original film. This contrast is shown as superimposed height profiles of the two kinds of films in Fig. 2c. The extended protruded structures have the typical granular morphology of Ppy, and the EDX result showed the presence of elemental nitrogen. Therefore, the extended structures can be identified as Ppy grown on top of the PEO domains originally present. After the regioselective nucleation of Ppy, its further growth occurred exclusively along the vertical direction for a period of about 2h, but the growth along horizontal directions is favored for a longer reaction time (> 2h), because it is known that the growth of Ppy is kinetically preferred on hydrophobic PS surfaces. Therefore, well-spaced Ppy domains, regioselectively grown on the immobilized FeCl₃ spinodal structures under 1 mM of pyrrole solution, were apparent only up to a reaction time of 2 h; longer reaction times (> 2 h) lead to the merge of the Ppy posts.

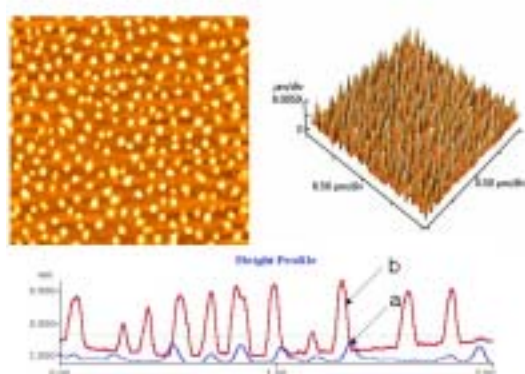


Figure 2. (a) Topological AFM image and (b) 3-dimensional AFM image of the spinodal structures formed by the polymerization of pyrrole on top of the PS-*b*-PEO film. (c) A superposition of cross-sectional AFM images of the spinodal structures before (marked a) and after (marked b) the growth of polypyrrole.

Under the standard ether medium, the growth of Ppy was preferred to the lateral direction as the reaction time is longer. However, when the cetyltrimethylammonium bromide (0.1 mM) was added into the standard medium, the lateral growth of Ppy was accelerated, and only thin films of Ppy without any spinodal structures were observed under 1 h reaction condition. However, when the silicon oil was added into the medium up to the volume ratio of 20 (silicon oil / ether), the Ppy grow exclusively to the vertical direction (Fig. 3a and b). Ppy can be grown up to the height of 33 nm (Fig. 3c) and the ratio (height/diameter) was increased up to 0.3 that was 3 times larger than that from the standard medium.

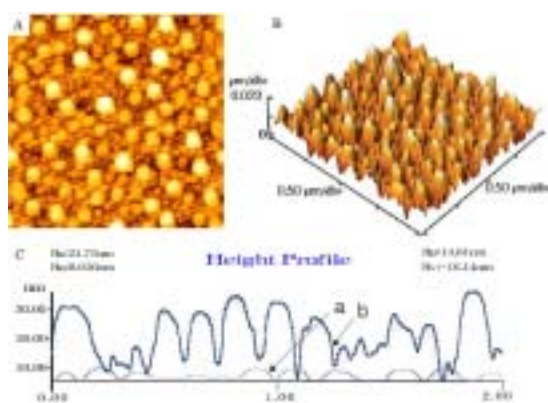


Figure 3. (a) Topological AFM image and (b) 3-dimensional AFM image of the spinodal structures formed by the polymerization of pyrrole on top of the PS-*b*-PEO film with silicon oil additives. (c) A superposition of cross-sectional AFM images of the spinodal structures before (marked a) and after (marked b) the growth of polypyrrole.

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