

Block Copolymer Thin Films: Nanotemplates for New Functional Nanomaterials

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Introduction

Nanoporous templates have been used for the fabrication of nanostructured materials that have their potential applications in electronics, optics, magnetism, and energy storage. Among many different types of self-assembled materials, block copolymers with well-defined nanoscopic structures have recently gained much attention for their potential uses as functional nanostructures.¹⁻³

We previously showed that the cylindrical microdomains in thin films of mixtures of polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) and PMMA homopolymers were oriented normal to the film surface, where the confinement of the PMMA homopolymer to the microdomains markedly enhance the aspect ratios of the microdomain orientation over ~ 10 times the bulk period (L_0).⁴ The whole PMMA phase or PMMA homopolymer itself were removed depending on the presence of UV irradiation, producing nanoholes, spanning the entire thickness of the film.

In this study, we employed porous nanotemplates prepared by block copolymer thin films for making high density array of conducting polymers and separation membrane for human rhinovirus 14 (HRV14), major causative agents of the common cold in humans, from phosphate-saline buffer (PSB) solution.

Experimental

Materials. PS-*b*-PMMA was prepared by using atom transfer radical polymerization as reported previously.⁴ The volume fraction of PMMA block was 0.30. The weight average molecular weight (M_w) and polydispersity index of the block copolymer were 55,500, and 1.19, respectively. Atactic PMMA homopolymer with $M_w = 31,800$ was purchased from Polymer Sources, Inc. An hydroxy end-functionalized random copolymer of styrene and methyl methacrylate, denoted PS-*r*-PMMA, having a styrene fraction of 0.6, was synthesized in bulk via a TEMPO living free radical polymerization.⁵ (M_w) and polydispersity index determined by size exclusion chromatography were 11,000, and 1.13, respectively.

Preparation of Nanoporous templates. We prepared block copolymer thin films by spin coating either on ITO glass or on ITO-coated flexible substrate such as polycarbonate. We removed either whole of PMMA phase by using UV etching or PMMA homopolymer alone without irradiation of UV etching followed by acetic acid rinsing. The pore diameter was $15 \sim 30$ nm determined by AFM (Digital Instruments Dimension™ 3100 SPM) in the tapping mode using silicon nitride tips on cantilevers (Nanoprobe) with a spring constant ranging from 40.0~66.0N/m and by field emission scanning electron microscopy (FE-SEM : Hitachi S-4600) operating at 120 kV.

Electropolymerization of Conducting Polymers. Polypyrrole (Ppy) was electrochemically polymerized at room temperature using 0.01 M pyrrole monomer in 0.001M lithium perchlorate in the propylene carbonate at -0.64 V. The working electrode was ITO glass on which nanoporous template was prepared. A Pt plate was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. Conducting polymer nanowires were grown from the ITO glass located at the bases of pores in the templates. The potential and exposure time for electropolymerization were carefully changed to optimize the height (~ 100 nm) of nanowires. Poly (3,4-ethylenedioxythiophene) (PEDOT) was also electropolymerized inside the nanoholes.

Preparation of Nanoporous Membrane for Virus Filtration. For the preparation of separation membrane for human rhinovirus 14 (HRV14), thin film of mixtures of PS-*b*-PMMA and PMMA homopolymer on silicon wafer with ~ 100 nm silicon oxide layer were immersed into 5 wt.-% HF solution, and floated onto

commercially available micro-filtration membrane for maintaining mechanical strength during filtration. Then, by immersing the film into acetic acid for 60 min, nanoporous templates were prepared. Permeation experiments were carried out in a dead-end ultrafiltration module (Amicon, 8010 stirred cell).

Plaque assay for detection of virus. A virus solution (5 ml) [5×10^6 PFU/ml in phosphate buffered saline (PBS)] was forced to pass through various filters, and then plaque assays were performed using solutions penetrated through the filters. HeLa/E cells were grown in a 35-mm petri dish with Dulbecco's modified eagles medium, 1% penicillin/streptomycin and 10% fetal bovine serum. The HeLa cells were washed once with PBS and once with a serum-free medium. An overlaying medium, composed of Dulbecco's modified eagles medium, 1% penicillin/streptomycin, 5% fetal bovine serum and 50% gum tragacanth, was added to the virus-infected cells, and then incubated for 3 days. After the virus cultivation, the overlaying medium was removed and then plaques were visualized with 0.5% crystal violet dissolved in 70% ethanol.

Results and Discussions

Figure 1 show FE-SEM images and AFM image of the nanoporous templates in the block copolymer films, from which we note that cylindrical pores were oriented normal to the substrates. Figure 1(a) show the FE-SEM image of a nanoporous block copolymer template on ITO glass, with cylindrical pores oriented normal to the substrate. These cylindrical pores can be perpendicular oriented on the conducting polymer layer as well as ITO glass. Also, as seen cross-sectional SEM image in Figure 1(b), the pores are seen to span the entire film thickness in the substrate. From Fast Fourier transform of images, the average center-to-center distance (λ_{CC}) between PMMA microdomains was ~ 46 nm. The pore diameter was ~ 20 nm.

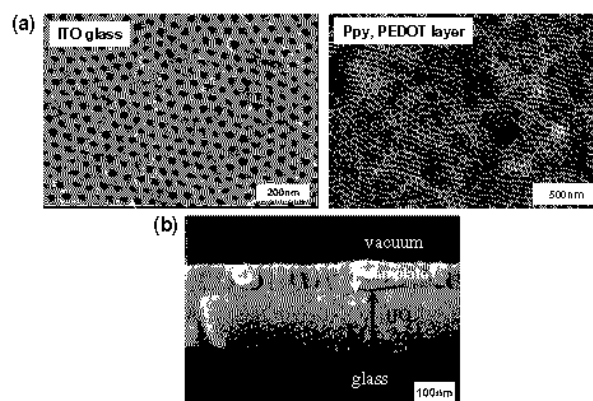


Figure 1. (a) FE-SEM image of nanoporous template prepared by PS-*b*-PMMA copolymer on ITO glass and conducting polymer film (b) Cross-section image of nanoporous template

Figure 2 shows top and cross-sectional views of FE-SEM images for nanowires of Ppy and PEDOT grown inside the nanoporous template. The crosslinked PS matrix was removed by combustion at 400 °C. In the case of nanotemplates prepared using the mixture of PS-PMMA and PMMA homopolymer, PMMA homopolymer was selectively removed by just washing with acetic acid. In this case, the block copolymer matrix could be easily removed by toluene. Figure 2(a) is the cross-sectional image of Ppy nanowires and PEDOT nanowires, from which the vertical oriented nanowires were clearly observed. It is noted in Figure 2(b) and Figure 2(c) that although the height of nanowires was uniform, the diameters of nanowires were similar to hole size of nanoporous template. Figure 2(b) is the image of PEDOT nanowires after removing crosslinked PS phase by combustion at 400 °C. And Figure 2(c) shows that top and cross-sectional images of PEDOT nanowires after removing the matrix of non-crosslinked phase just by rinsing in acetic acid because nanoporous template was made by removal PMMA homopolymer. The height of the nanowires grown inside nanoporous templates was about 50 nm \sim 100 nm.

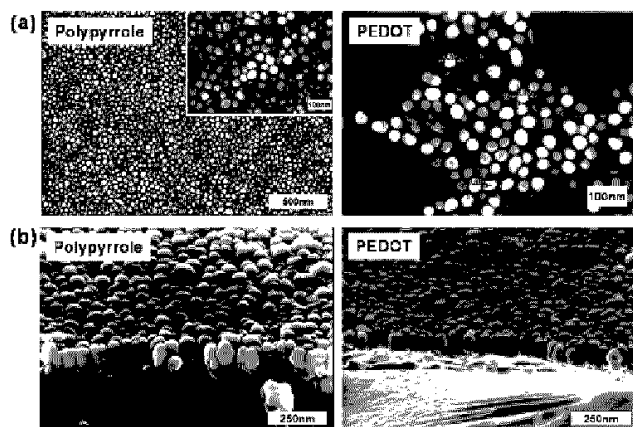


Figure 2. FE-SEM images of top view and cross-sectional view of the polypyrrole and PEDOT nanowires grown inside the nanoporous template (a) top images of Ppy and PEDOT nanowires (b) cross-sectional images of Ppy and PEDOT nanowires; the matrix of crosslinked PS phase was removed by combustion at 400 °C.

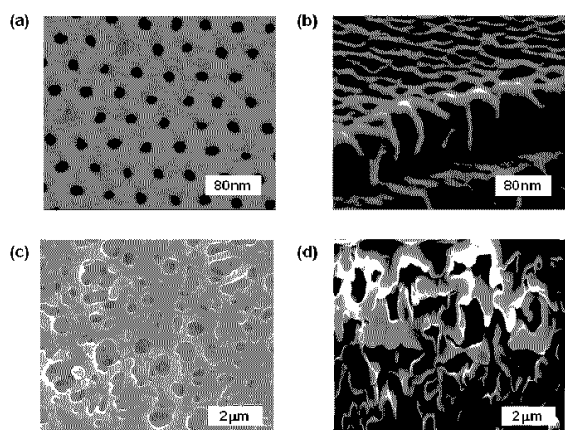


Figure 3. Top (a, c) and cross-sectional (b, d) SEM images for the top layer made of nanoporous block copolymer (a and b) and PSU supporting membrane (c and d).

Figure 3 (a) and (b) give top and cross-sectional SEM images, respectively, for nanoporous thin film prepared by PS-*b*-PMMA and homopolymer PMMA mixture. It is seen that cylindrical nanopores are oriented normal to the substrate and all pores touch the substrate. This thin film was used for the separation for the HRV 14 virus. Since the film was too thin, it is not useful for the separation membrane. Thus, an additional supporting membrane made of polysulfone (PSU) was employed. The pore size in PSU membrane was 0.2 µm, and the pore area is much larger than that in block copolymer thin film, as shown in Figure 3(c, d). Therefore, the flux and the selectivity of virus solution depend exclusively upon the top layer, not on the PSU membrane.

Conclusions

Conducting polymer nanowires of Ppy and PEDOT with high areal density ($\sim 10^{11}$ pores/cm²) were successfully prepared by using block copolymer nanoporous template onto ITO glass and conducting polymer layer. This template could be used as novel membrane showing high flux without sacrificing selectivity for the separation of HRV 14.

Acknowledgements

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