Fabrication of Conducting Polymer Nanowires using Block Copolymer Nano-porous Templates for Photovoltaic Device

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Introduction

Self-assembled nano-structured materials consisted of organic, inorganic, and polymeric compounds have been extensively investigated. 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] Here, we show that nanoporous templates made from polystyrene-*block*-poly(methyl methacrylate) (PS-b-PMMA) satisfy a novel design concept. Previous studies have shown that arrays of nanoscopic cylindrical microdomains oriented normal to the surface of the film can easily be prepared.[2-4] We prepared ultra high density arrays of conducting polymer as poly(pyrrole) (Ppy) and poly(3,4-ethylenedioxythiophene) (PEDOT) nanowires with diameters of 25 ~ 40 nm on the ITO glass by electropolymerization of the monomers inside nanoholes. These high density arrays of conducting polymer nanowires could be used as P-type materials for photovoltaic devices.

Experimental

PS-b-PMMA was prepared by using atom transfer radical polymerization as reported previously. Volume fraction of PMMA block was 0.30. The weight average molecular weight (Mw) and polydispersity index of the block copolymer were 55,500, and1.19, respectively. Atatic PMMA homopolymer with Mw = 31,800 was purchased from Polymer Sources, Inc.

We prepared block copolymer thin films by spin coating either on ITO glass or conducting polymer layer. After confirming that PMMA microdomains were aligned normal to the substrate, only homopolymer portion was etched out by using a selective solvent of acetic acid. The pore diameter was ~ 20 nm determined by AFM (Digital Instruments Dimension™ 3100 SFM) in the tapping mode using silicone 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-4200) operating at 120 kV.

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 film was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. Current change with time was recorded using a potentiostat controlled by PowerLab/4SP (ADInstruments). PPy nanowires were grown from the ITO glass located at the bases of pores in the templates. The potential and exposure time for electropolymerization was chosen to optimize the height (~ 100 nm) of Ppy nanowires. The other conducting polymers, poly(3-hexyl thipene) and poly (3, 4-ethylenedioxythiopene), were also electropolymerized inside nanoholes.

Results and discussion

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.

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 ~ 100 nm.

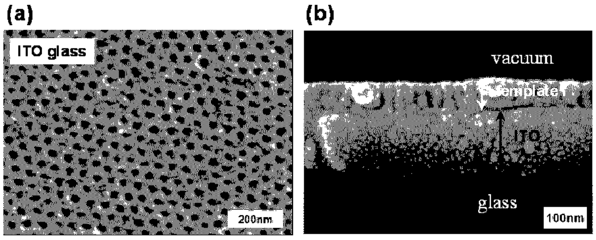

Figure 1. (a) FE-SEM image of nanoporous template prepared by PS-b-PMMA copolymer on ITO glass (b) Cross-section image of nanoporous template

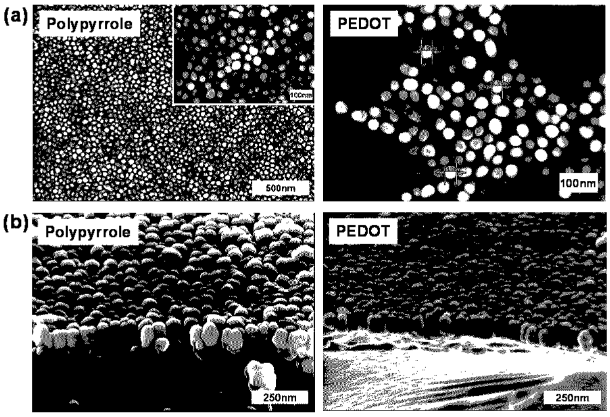

Figure 2. FE-SEM images of top view and cross-sectional view of the polypyrrole and PEDOT nanowires grown inside the nanoporous template (a) top images of Ppy and PEDOT nanowires (b) cross-sectional images of Ppy and PEDOT nanowires; the matrix of crosslinked PS phase was removed by combustion at 400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

Conclusions

Nanoporous templates were successfully prepared from PS-b-PMMA on the ITO glass and conducting polymer. Conducting polymer nanowires with high areal density (~ 10^{11} pores/cm^2), was also prepared by electrochemical polymerization within this template. These nanowires prepared using block copolymer nanoporous template have potential use as photovoltaic devices.

References

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