

Highly Aligned Ultrahigh Density Arrays of Conducting Polymer Nanorods using Block Copolymer Templates

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ABSTRACT

Ultrahigh density arrays of conducting polypyrrole (PPy) nanorods are fabricated directly on the indium–tin oxide coated glass by an electropolymerization within a porous diblock copolymer template. The nanorods are shown to have conductivity much higher than thin PPy films, due to the high degree of chain orientation, even though the separation distance for two neighboring PPy main chains is as small as 0.37 nm. The ultrahigh density arrays of conducting polymer nanorods have potential applications as sensor materials, nanoactuators, and organic photovoltaic devices.

Nanoporous templates have been used for the fabrication of nanostructured materials that have potential applications in electronic, optical, magnetic, and energy storage devices.^{1–12} Both track-etched polymer membrane and anodized aluminum oxide (AAO) membrane have been widely used to prepare conducting polymer nanotubes and nanowires. The former contains randomly distributed nanochannels with an areal density of the only $\sim 10^9$ pores/cm² which precludes the fabrication of ultrahigh density arrays of conducting polymer nanorods.^{1–8} With the AAO membrane well-defined arrays of poly(3,4-ethylenedioxythiophene) (PEDOT) nanotubes have been prepared by electrochemical polymerization,⁹ and nanotubes and nanowires of polypyrrole and poly(3-methylthiophene) have also been synthesized.^{10,11} However, upon removal of the AAO matrix the array of nanotubes (or nanowires) collapse onto the substrate, losing their orientation. Thus, it is not easy to obtain the arrays of nanotubes

(or nanowires) standing vertically on a substrate after removing the templates. Although the conductivity of conducting polymer nanotubes (or nanowires) inside the templates was measured,^{1–5} the conductivity of individual nanorod on a substrate without templates was not measured. Recently, without using templates, conducting polymer nanofibers and nanorods are also prepared by electrochemical synthesis¹³ or chemical oxidative polymerization.¹⁴

The use of block copolymers as templates and scaffolds for the fabrication of nanostructured materials has drawn significant attention recently.^{15,16} External fields, like an applied electric field^{17–19} or solvent evaporation,²⁰ or internal fields, as with the addition of a homopolymer that is miscible with the minor component,^{21,22} have been used to orient the microdomains of block copolymers to generate arrays with areal densities in excess of 10^{11} elements per square centimeter. Upon removal of the minor component, nanoporous templates are produced that can be used for pattern transfer,^{23–25} separations media for viruses,²⁶ or as templates for surface chemistry²⁷ or electrodeposition to generate arrays of metal nanowires.^{18,19} On the other hand, Li et al.²⁸ employed polystyrene-*block*-poly(4-vinyl pyridine) copolymer monolayer micelle films to fabricate polyaniline nanofibers on a gold-coated silicon substrate by electropolymerization. However, since the template was based on the

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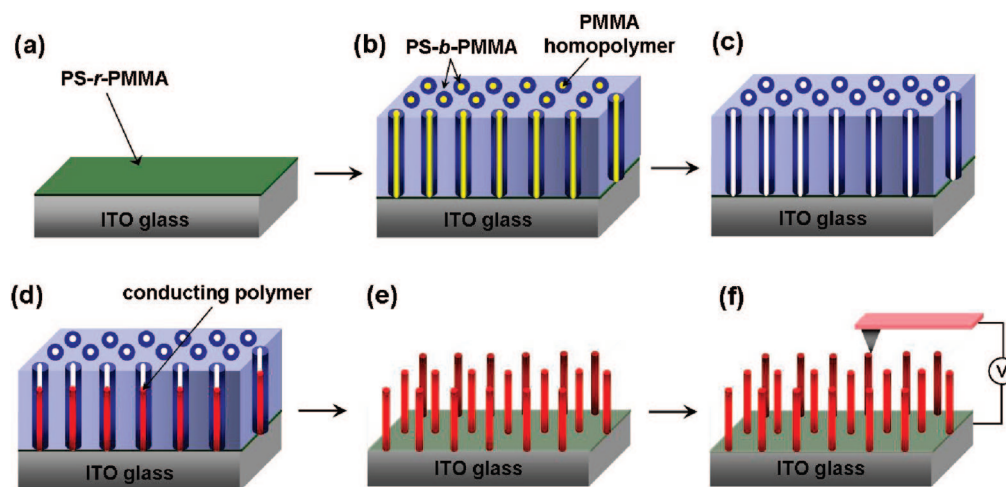


Figure 1. Fabrication of ultrahigh density array of conducting polymer nanorods with block copolymer nanoporous templates.

monolayer of micelle structure, the maximum thickness of the templates was at most 30 nm. To obtain nanofibers (or even nanorods) of polyaniline, these should be overgrown outside the template; thus the structure was not individual nanowire (or nanorods), but randomly intermingled nanowires. It is well-known that, when polymer chains are confined into nanosized holes, they are highly aligned to the template length direction. Since the conductivity of the conducting polymers depends strongly on the alignment of the polymer chains, it is necessary that the chains should be highly aligned to the thickness direction. Since the individual and well-aligned nanostructure cannot be obtained using the block copolymer micelle template, the cylindrical nanoholes templates with a thickness of ~ 120 nm (or larger) are required. Furthermore, the cylindrical nanoholes could be obtained on transparent substrates such as the ITO-coated glass, which is useful for optoelectronic application as solar cell or sensor.

Here, we show the preparation of ultrahigh density arrays of nanorods of a conducting polymer, polypyrrole (PPy), on ITO-coated glass in a nanoporous template, prepared from a block copolymer of polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA), by electropolymerization within the template. High resolution transmission electron microscopy (HR-TEM) shows that the main chains of PPy are aligned along the nanorod direction. The conductivity of a single PPy nanorod was measured using current-sensing atomic force microscopy (CS-AFM) and it was much higher than that of continuous PPy film.

Figure 1 shows a schematic diagram of the process used to fabricate ultrahigh density arrays of conducting polymer nanorods with a nanoporous template generated from a block copolymer. Details of experimental procedures and characterization methods are shown in Supporting Information S1. First, a hydroxy terminated random copolymer of styrene and methyl methacrylate (PS-*r*-PMMA), having a styrene weight fraction of 0.58 and a number-average molecular weight of 11 000, was spin coated onto an ITO-coated glass. This random copolymer was anchored to the ITO to balance interfacial interactions so as to aid the orientation of the PMMA microdomains normal to the substrate. After washing

out the unanchored random copolymer by toluene, the random copolymer brush with ~ 6 nm thickness was anchored onto the ITO. At the second step, a mixture of poly(methyl methacrylate) (PMMA) homopolymer and PS-*b*-PMMA was spin coated onto a random copolymer-coated ITO glass producing a film with a thickness of ~ 120 nm. PMMA homopolymer was removed by extraction with acetic acid, a selective solvent for PMMA. While UV irradiation can be used to remove the PMMA block of the copolymer,¹⁸ the PS matrix is cross-linked making it necessary to use temperatures in excess of 450 °C to completely remove the PS, which may adversely affect the electrical properties of the nanorods. The conducting polymer was grown from the base of nanoholes by electropolymerization producing an ultrahigh density array of conducting polymer nanorods oriented normal to the substrate. By using toluene, the PS-*b*-PMMA matrix was completely removed, leaving self-supporting arrays of conducting polymers oriented normal to the substrate surface. Topographic and current images and *I*–*V* curves were measured using CS-AFM.

Figure 2a,b gives top and cross-sectional field emission scanning electron microscopy (FE-SEM) images of a nanoporous block copolymer template on ITO glass, indicating that cylindrical pores oriented normal to the ITO glass span the entire film from the surface to the substrate. Two different views of the free-standing array of conducting polymer (PPy) nanorods grown in the block copolymer scaffold are shown in Figure 2c,d. Here, the block copolymer matrix was completely removed by rinsing with toluene. It is seen that a high density array of vertically aligned PPy nanorods was maintained after removing the matrix, although the height and the areal (or spatial) density of the PPy nanorods are not perfectly uniform because of the nature of the electropolymerization for conductive polymers inside nanoporous templates, as reported in the literature.^{4,5,7} The height of the nanorods grown inside nanoporous templates was controlled by the time used in the electropolymerization under the constant voltage (see Figure S1a in Supporting Information). It should be noted that the conducting polymer nanotubes, not nanorods, were formed when the pore sizes of the

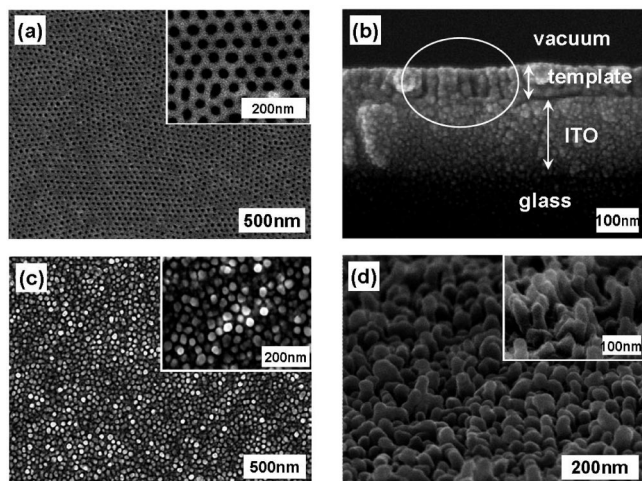


Figure 2. FE-SEM images of nanoporous templates prepared by PS-*b*-PMMA/PMMA mixture film on the ITO glass and PPy nanorods. (a) Top and (b) cross-sectional images of the nanoporous template. (c) Top and (d) cross-sectional images of PPy nanorods after removing the template.

templates were larger (more than 50 nm).^{5,9} The nanorods were formed because of the smaller diameter (~ 25 nm) of the block copolymer template.

It is noted from Figure 2a–d that the diameter of PPy nanorods looks slightly larger than that of nanoholes in the templates. To verify this change, we obtained the scanning probe microscopy (SPM) and FE-SEM images of nanoporous templates before and after electropolymerization, given in Figure S2 of the Supporting Information and Figure 2a,c. A slight swelling of nanoholes was observed during the electropolymerization, which results in slight increase (less than 5 nm) in the diameter of PPy nanorods compared with template diameter (the insets in Figures 2a,c, and Figure S2).

A schematic diagram of CS-AFM is shown in Figure 3a, along with the I – V curves of PPy nanorods and a PPy film in Figure 3b, from which the current flowing at a given bias voltage for the PPy nanorods is ~ 3.6 times that of the film. The thickness for PPy film and nanorods are the same (~ 100 nm). Also, a random brush (with 6 nm thickness) grafted ITO was used for preparing both PPy film and PPy nanorods. We consider that the I – V curve for the nanorods represents a characteristic curve for a single nanorod, because the contacting diameter of CS-AFM probe employed in this study is 20–30 nm.²⁹ To the best of our knowledge, these are the first measurements on a single conducting polymer nanorod oriented perpendicular to a substrate. Figure 3c,e is SPM height images of PPy nanorods and the film, respectively. The bright spots in tapping mode SPM height image are PPy nanorods. Figure 3d,f are the current images of PPy nanorods and the film. It is seen that the current image of continuous PPy film indicates that PPy covers the entire surface, while that of the PPy nanorods shows that the current flows only through the PPy nanorods. PPy nanorods appearing as the bright spots in tapping mode SPM height image are consistent with those in the current image. It is seen in Figure 3d that the current of the continuous PPy film was not uniform. This is because it was prepared by electropo-

lymerization. In this situation, the film surface could not be perfectly uniform. Thus, depending upon surface roughness, the conductivity can vary with position. Similar observation was reported in the literature.^{30,31}

The average current flowing through the nanorods was 253 nA (with the standard deviation of the current of 84 nA, obtained from 380 PPy nanorods) at a given bias voltage of 0.2 V, which is 3.6 times that (70 nA) of the film. We consider that the somewhat large standard deviation of the current of the PPy nanorods is attributed to nonuniform heights of the PPy nanorods, arising from the electropolymerization for conductive polymers inside the nanoporous templates, as reported in the literature.^{4,5,7} From Figure 3b,d,f, the conductivity of the PPy nanorods is significantly higher (by more than a factor of 3) in comparison to that of the film.

We also employed a 2-point probe experiment to compare the conductivity of PPy nanorods with the film covering a large area. For this purpose, we prepared the sample as follows. PPy nanorods are electropolymerized in the nanoporous block copolymer template, and the height of nanorods is carefully controlled so that the length of PPy nanorods should be smaller than the template thickness. Then, the top of the block copolymer template, which does not contain the nanorods, was very carefully removed by O_2 plasma etching, so that the ends of the PPy nanorods are open to the air. It is noted that the block copolymer template was not removed by toluene for this purpose, since evaporated gold might fill up the gap between the PPy nanorods. After we prepared the array of gold electrodes with the area of each electrode being 6.0×10^{-4} cm² by evaporating Au on the top of the template using a patterned grid, 2-point probe measurement (HP5270A) was performed. It is noted that the probe diameter was 10 μ m, much smaller than each gold electrode. We performed at least 10 experiments. From the slope of current versus voltage (I – V) curve, the conductance (C) is measured, and the conductivity σ is obtained from eq 1:

$$C = \frac{I}{V} \quad \sigma = C \times \frac{L}{A} \quad (1)$$

The height (L) of the PPy film and nanorods are the same (100 nm), and the area (A) for the continuous film is the same as the area of each Au electrode. But A (area) for nanorods in the block copolymer template is defined as the area of each Au electrode multiplied by 0.25, which is obtained from the top view FESEM image. It is noted that a random brush (with ~ 6 nm thickness) grafted ITO was used for preparing both samples. Figure 4 gives the I – V curves for PPy continuous film and nanorods. Although the conductance of the nanorods is smaller than that of the continuous film, the area of A for the former is four times smaller than that for the latter. Thus, the conductivity (10.48×10^{-4} S/cm) of PPy nanorods is ~ 3.0 times higher than that (3.6×10^{-4} S/cm) of PPy continuous films, consistent with the results given in Figure 3. Furthermore, we observed that PEDOT nanorods prepared from block copolymer template have a higher current and therefore conductivity

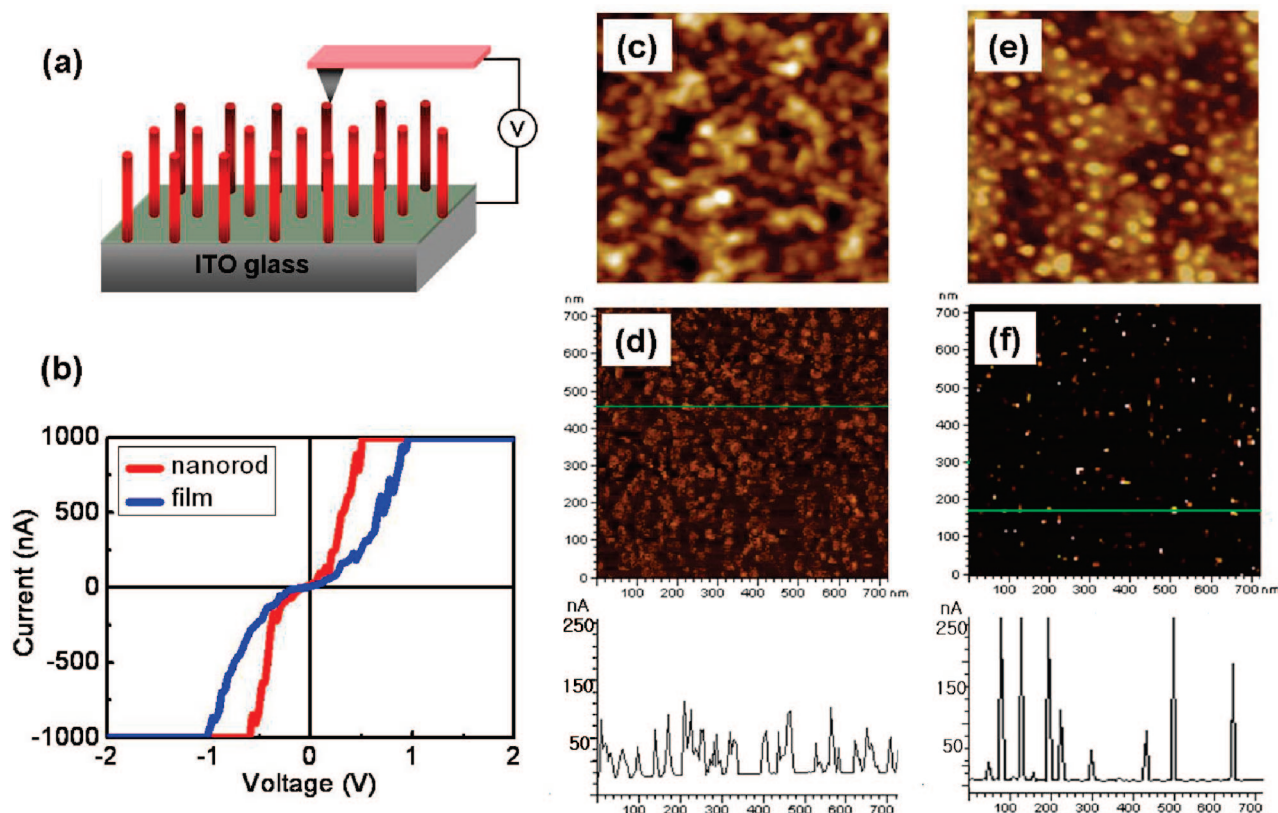


Figure 3. Current-sensing AFM images of PPy film and nanorods. (a) The schematic of CS-AFM for PPy nanorods; (b) I - V curves of PPy film and PPy nanorods; (c) and (e) SPM height images of the PPy film and PPy nanorods; (d) and (f) current images (top) and profile (bottom) of the PPy film and PPy nanorods.

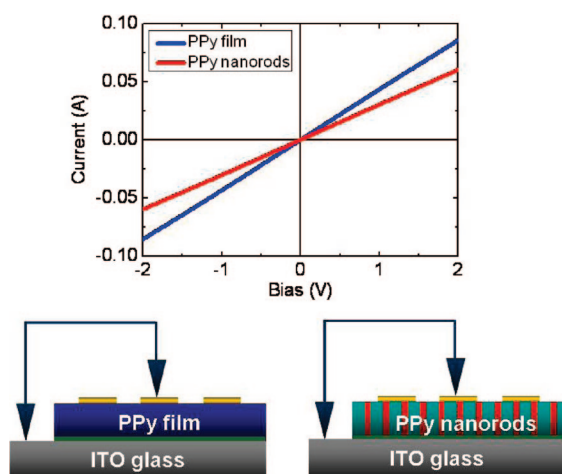


Figure 4. I - V curves for PPy continuous film and PPy nanorods and the schematic of 2-point probe measurement.

(~ 5 times) in comparison to a continuous PEDOT film (see Supporting Information S4). It is noted that the measured conductivity of PPy nanorods (or film) is much smaller than that reported by Demoustier-Champagne and Stavaux.⁷ However, the conductivity of a conducting polymer prepared by electropolymerization depends greatly on experimental conditions, such as water content in the solution and the type of dopant, and the concentrations of monomer and dopant.^{7,31} The concentration (0.001 M) of dopant employed in this

study is much lower compare to that (~ 0.1 M) in ref 7 in addition to using different solvents. The conductivity obtained in this study has a similar order of the magnitudes to that reported in the lieterature.³²

Many research groups reported that conducting polymer nanowire show a higher conductivity in comparison to thin films.^{1-4,10} But, to the best of our knowledge, the conductivity measurement of a vertical oriented single conducting polymer nanowire has not been directly measured. In general, it has been simply assumed that the higher conductivity arises from a chain orientation along the axes of the rods without further quantification of individual nanorod (or nanowire) standing on a solid substrate. Some research groups used polarized infrared (IR) absorption spectroscopy to determine the molecular chain alignment of the conductive polymer nanorods and nanowires.²⁻⁶ However, in this study, we could not use polarized IR absorption spectroscopy to determine chain orientation of PPy nanorods because the absorption peak of polypyrrole nanorods themselves was not detected in the IR wavelengths due to very strong absorbance of ITO substrate in the IR wavelengths. Thus, HR-TEM and grazing incidence X-ray diffraction (GIXD) experiments are performed on the PPy nanorods. HR-TEM images of the PPy nanorods and PPy continuous film are shown in Figure 5a-d. The diameter and height of PPy nanorods measured from Figure 5a are 25 and 95 nm, which are consistent with those from the FE-SEM image (see the inset of Figure 2d).

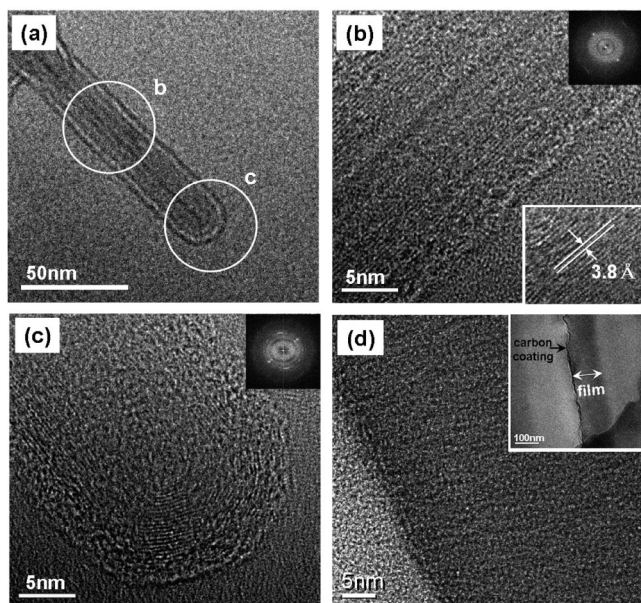


Figure 5. High resolution TEM images of PPy nanorods (a–c) and PPy continuous film (d). (a) At low magnification. (b–d) High magnification.

Moreover, the height of PPy nanorods seen in Figure 5a is also consistent with SEM image obtained from focus-ion-beam method, as shown in Figure S3 of Supporting Information. In this study, we prepared the PPy nanorods with a height of ~ 100 nm because this height is similar to the optimum thickness for highly efficient organic photovoltaic devices.³³

In Figure 5a, a single nanorod is seen, and the orientation of the PPy is maintained along the length of the nanorods, that is, the growth direction, as evidenced by the appearance of only two spots in the electron diffraction pattern (inset of Figure 5b). It is noted that this extent of orientation is seen in all the PPy nanorods, as shown in Supporting Information Figure S4. On the other hand, PPy films do not have such orientation, as shown in Figure 5d. The PPy film was prepared by electropolymerization under the same conditions as employed for PPy nanorods. The distance between two neighboring lines in HR-TEM (inset of Figure 5b) is 0.38 nm, which is identical to the π – π stacking distance (0.38 nm) for poly(3-hexyl thiophene) (P3HT) conducting polymer.³⁴ Even though there have been no reports on the π – π stacking of PPy main chains, such packing should be expected by the confinement of the PPy chains inside the nanoporous templates with a diameter of ~ 25 nm.

It is seen in Figure 5b,c, some portions of nanorods near the wall look well-aligned along the thickness, while they are not near the center. However, the nanorods are solid, not hollow nanotubes. Interestingly, a fingerprint pattern is observed near the end of the nanorods. It is well-known that the block microdomains easily form sheet-like structures when these are confined geometrically.^{35,36} If the nanotubes are synthesized inside the nanopores, straight and opened structures would be observed. However, in the case of

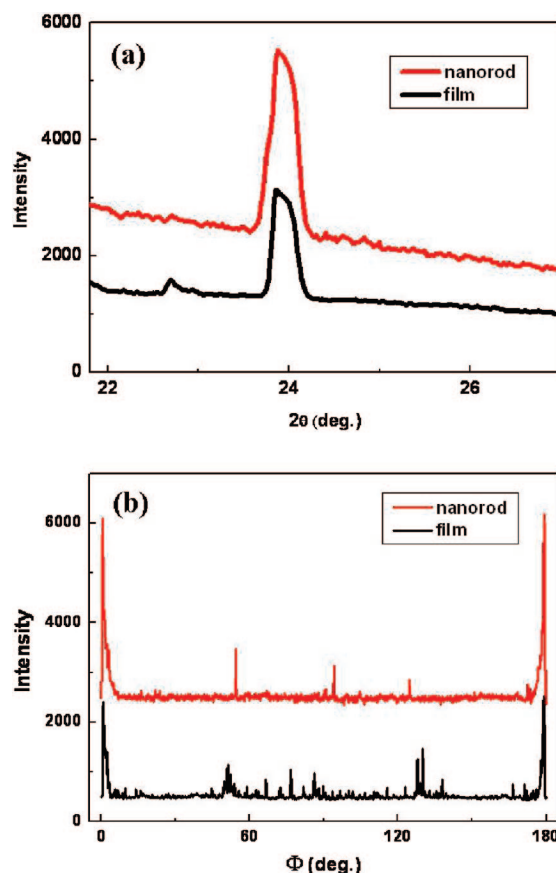


Figure 6. (a) In-plane X-ray diffraction profile and (b) azimuthal angle dependence of X-ray diffraction at $2\theta = 23.8^\circ$ of PPy nanorods and continuous film.

nanorods that the end is closed, it is very difficult for the polymer chains to be straight at the end, suggesting that a bent structure is more favorable than a straight one. Although the exact origin of the fingerprint pattern is not known at this stage, we speculate that it arises from the preferential growth of the PPy chains along the wall of the pores and interfacial tension between the wall and the polymer chains. Stucky and co-workers demonstrated that lamellar (planar) layers were scrolled into coaxial multilayer cylindrical structures when they are confined.³⁵ In this situation, a fingerprint pattern formed at the end of the rods. A similar fingerprint pattern with convex shape near the top was observed for the lamellar microdomains of polybutadiene block in polystyrene-*block*-polybutadiene copolymer when it was confined into the AAO template,³⁶ although the size of the microdomain (~ 20 nm) was much larger than that (~ 0.38 nm) seen in this study. Also, a similar fingerprint pattern was observed when multiwalled carbon nanotubes were grown from a FeCO crystal.³⁷

Figure 6a shows the in-plane X-ray diffraction profile covering 2θ from 21 to 27° , focusing only on the π – π stacking peak of PPy chains, for PPy nanorods and a continuous PPy film. For this purpose, we employed the grazing incidence X-ray diffraction (GIXD) experiment with a synchrotron source in beamline 5A of Pohang light source. The exposure time was 100 s with an increment of $2\theta =$

0.02°. Here, we clearly see the π - π stacking peak at $2\theta = 23.8^\circ$, corresponding to the PPy interchain distance of 0.37 nm, for both PPy nanorods and PPy film. The value of 0.37 nm is almost the same as that (0.38 nm) obtained from HR-TEM (the inset of Figure 5b).

To determine the orientation of PPy chain, we obtained the azimuthal-angle (ϕ) dependence of X-ray diffraction at $2\theta = 23.8^\circ$ of PPy nanorods and PPy film, as shown in Figure 6b. It is noted that, when PPy chains are oriented perfectly along the nanorod axis (or thickness direction), only in-plane X-ray diffraction ($\phi = 0$ and 180°) is observed.

From Figure 6a, the in-plane X-ray diffraction intensity of the PPy nanorods are clearly larger than that of the PPy continuous film. Furthermore, it is seen in Figure 6b that the X-ray diffraction intensity at $\phi = 0$ (and 180°) of the PPy nanorods is very large and distinct, though small side peaks are observed near $\phi = 54, 94$, and 125° . Small side peaks might arise from the fingerprint pattern observed near the end of the PPy nanorods (Figure 5c). On the other hand, many peaks are observed at various ϕ for the continuous PPy film, indicating that PPy chains in the film have many different orientations. Thus, we conclude that the alignment of PPy chains along the growth direction of the nanorods is much enhanced compared with the PPy continuous film.

The results shown in this study demonstrate that nanoporous templates made from block copolymers are very effective means of fabricating conducting polymer nanorods with a high alignment of polymer chains and an enhanced conductivity along the nanorod axes, that is, the growth direction of the polymerization. Nanoporous templates from PS-*b*-PMMA with the cylindrical microdomain morphology could be prepared directly on a conducting substrate, ITO glass, with an areal density $\sim 10^{11}$ pores/cm². A similar approach can be used to prepare PPy, PEDOT, and P3HT nanowire arrays on flexible substrates, like ITO-coated polycarbonate and poly(ethyleneterephthalate) thin films, which greatly expands the utility and versatility of this process. These ultrahigh density arrays of conducting polymer nanorods have applications as sensor materials, nanoactuators, and organic photovoltaic devices.

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Supporting Information Available: Details on the experimental procedure for the fabrication of nanoporous templates from block copolymers and electropolymerization

of nanorods inside the nanoporous template and several supporting images. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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