Electrochemical Synthesis and Fast Electrochromics of Poly(3,4-ethylenedioxythiophene) Nanotubes in Flexible Substrate

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There has been much work on the development of conducting polymer-based electrochromic devices for sensors, smart mirrors and windows, signal transduction, and flexible displays since these devices have many attributes such as flexible, thin, low-power consuming, lightweight, and inexpensive devices.[1−3] Poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives are especially one of the most attractive electrochromic materials of conducting polymers due to the high contrast ratios as well as an availability of diverse colors.[4−6] One of the important issues in the electrochromic devices is the color-switching rate as well as the color contrast.[4,5] The fast electrochromic response can be achieved by reducing the film thickness since the color-switching rate is determined by the diffusion rate of counterions into the film during the redox process. However, this leads to insufficient coloration and color contrast of the electrochromic device.

Recently, we have pioneered the electrochromics of nanotubular structure of PEDOT and could achieve the extremely fast electrochromic response (less than 10 ms) without sacrificing the color contrast.[7] The PEDOT nanotubes were synthesized electrochemically in the pores of the alumina template film at high reaction potential and low monomer concentration based on the new proposed mechanism.[7] The thin nature of the nanotube wall decreased the diffusion time of counterions dramatically, thus the electrochromic response time and the controlled length of PEDOT nanotube arrays in the porous alumina film gave the strong coloration and color contrast. However, there is a problem in fabricating a flexible electrochromic device using the alumina template due to its fragility.

Track-etched porous polycarbonate (PC) membrane is a good candidate for the flexible template. This membrane is very flexible, commercially available with various pore diameters (0.01−20 μm), and quite transparent due to the thin film thickness (6−10 μm). Although there have been a few studies on the electrochemical synthesis of conducting polymer nanotubes using template synthesis,[7−10] Duvail et al. have recently reported that PEDOT in a PC membrane, unlike polypyrroles and polyanilines, was likely to be electrochemically synthesized as nanowires (nanofibrils) instead of hollow nanotubes.[11] This was attributed to the difference in the interaction of pore wall with nascent polymers. Thus, the electrochemical synthesis of PEDOT nanotubes is still challenging in the porous PC membrane. Here, we describe a new electrochemical synthetic method and characterization of PEDOT nanotubes in the PC membrane. The well-defined nanotubular structure provides fast electrochromic response (20 ms for decoloration or oxidation) in the highly flexible substrate.

Figure 1 illustrates the schematic for the electrochemical synthesis of the PEDOT nanotubes in the pores of PC membrane. One side of the PC film (220 nm pore diameter) was sputter-coated with a thin layer of gold as a working electrode for the electrochemical synthesis of PEDOT nanotubes in each of the membrane pores. The key controlled variables in nanotube synthesis are applied potential, monomer concentration, and electropolymerization time. In particular, electropolymerization time was adjusted to control the length of PEDOT nanotubes. Polymerization was performed potentiostatically at different potentials of 1.2, 1.4, 1.6, and 1.8 V versus Ag/AgCl in an acetonitrile solution of 10 or 25 mM in 3,4-ethylenedioxythiophene (EDOT) and 100 mM in $LiClO_4$.

Since the thin wall thickness of tubular structure is the essential part to achieve the fast electrochromic response, PEDOT nanotubular structures were characterized with transmission electron microscopy (TEM) after the removal of the PC template. We attempted to synthesize PEDOT nanotubes at a low monomer concentration (10 mM) and high potential (1.8 V), based upon previous experimental condition.[7] However, an undesired reaction such as the dissolution of the gold electrode was involved in this condition, which made it difficult to synthesize PEDOT nanotubes. At the potentials of 1.6 V, we obtained partially filled nanotubes (Figure 2a) instead of the complete nanotubular structures obtained previously in the alumina template. This result may be caused by the difference in the

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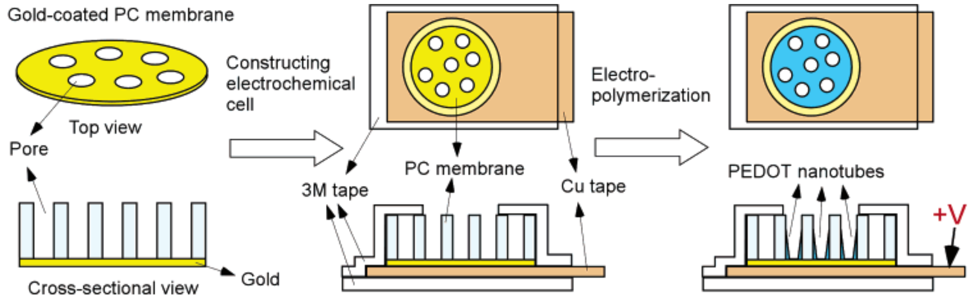

Figure 1. Schematic of fabricating PEDOT nanotubes on a flexible template.

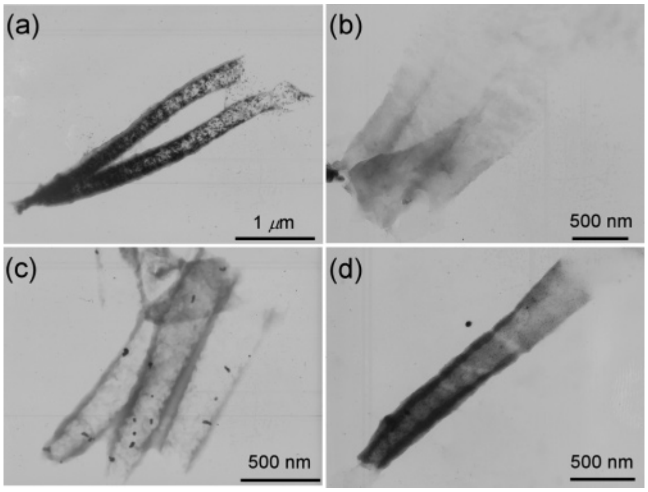

Figure 2. TEM images of PEDOT nanotubes synthesized in a PC membrane at different conditions: (a) 10 mM EDOT, 1.6 V, 40 s; (b) 10 mM EDOT, 1.2 V, 40 s; (c) 25 mM EDOT, 1.2 V, 40 s; (d) 25 mM EDOT, 1.2 V, 80 s. The outer diameter of nanotubes (more than 300 nm) in panels b and c is larger than expected (ca. 220 nm). This can be ascribed to the collapse of nanotubes after removing the template due to the very thin nature of PEDOT nanotubes and also to the cigar shape of pores in the template.

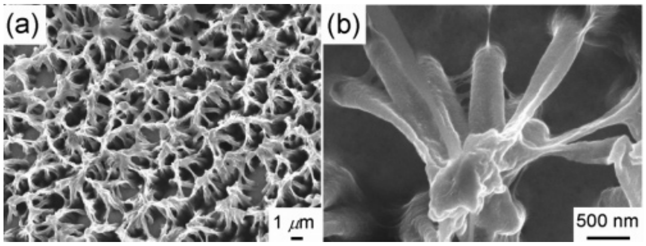

Figure 3. SEM images of PEDOT nanotubes after removing a template: (a) low and (b) high magnification. Experimental conditions are the same as with Figure 2d.

properties of the membrane and the bottom electrode. The filled portion of the nanotube was increased by lowering the potential to 1.4 V, as predicted from the previous report,[7] since the reaction rate was decreased while the monomer diffusional flux was about the same into the pores. The increase of filled portion deteriorates the color-switching rate significantly in an electrochromic device. Interestingly, nanotubes with very thin wall thickness (less than 10 nm in thickness) were obtained at the lower potential, 1.2 V (Figure 2b). This phenomenon contradicts the previously proposed mechanism that nanowire structure is preferably obtained as the reaction potential decreases.[7] This might be explained by a preferable polymerization reaction on the ring-shaped gold electrode end at the bottom of pore (see Supporting Information). The ring-shaped electrode end may serve as an electrochemical active site at the low onset oxidation potential,[12−14] because the oxidative polymerization of EDOT starts about at 1.2 V.[6] We are still investigating this explanation in more detail.

At a higher concentration such as 25 mM EDOT, the thicker nanotubes were obtained at 1.2 V for 40 s as expected (Figure 2c). Longer and thicker nanotubes (~2.5 μm long; ca. 50 nm thick in the middle of nanotube) were obtained at 1.2 V for 80 s in 25 mM EDOT in an acetonitrile solution (Figure 2d). Further increasing the electropolymerization time to 300 s led to completely filled nanowires. It is worth noting that the nanotube wall becomes thinner at the top with respect to the growth axis of the nanotube in Figure 2c,d. This can be attributed to the diffusion of monomers from the bulk solution to the bottom over the time of nanotube growth after consuming the monomers present in the beginning as described previously.[7]

The tubular structures could also be proved using scanning electron microscopy (SEM). After removing the polycarbonate template using methylene chloride, SEM images were taken for PEDOT nanostructures synthesized at 1.2 V for 80 s in 25 mM EDOT. The low magnified image shows the aggregated and collapsed PEDOT nanostructures (Figure 3a). This phenomenon seems to be caused by the surface tension generated at the interfaces between nanotube surfaces and liquid during the evaporation of solvent. The wrinkled and collapsed structures of the nanotubes are much more clear in the high magnified image (Figure 3b), which strongly supports that the inside of nanostructures is empty. Due to the very thin nature of PEDOT nanotubes, they could not retain their shapes after removing the template.

Figure 4 shows nanotube wall thickness changes as a function of electropolymerization time. Here, the wall thickness was measured at the middle of PEDOT nanotubes. These results may explain those of Duvail et al.,[11] the preferred growth of nanowire structure of PEDOT in a PC membrane, because they used the longer electropolymerization time (400 s) in the smaller pore size (150 nm) of PC membrane. We obtained the nanotubular structure of PEDOT based on Duvail et al's condition with the shorter polymerization time (100 s, see Supporting Information).

To demonstrate the fast color change of a nanotube-based electrochromic device, an electrochemical cell was con-

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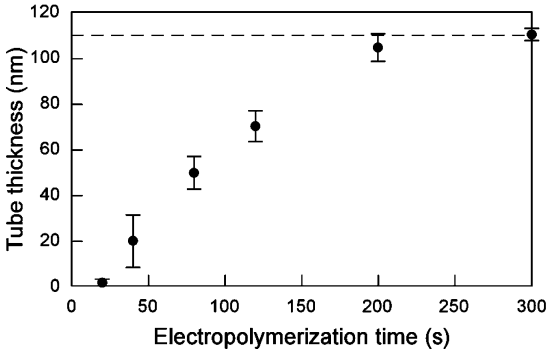

Figure 4. Plot of nanotubular wall thickness as function of electropolymerization time in 25 mM EDOT at 1.2 V. The dashed line represents the completely filled nanotubes (e.g., nanowires).

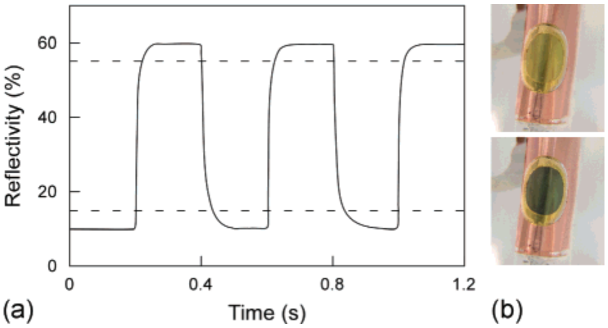

Figure 5. (a) Plot of reflectivity of electrochromic window monitored at 600 nm for coloration and decoloration upon potential switching between −1.0 and 1.0 V. The dashed lines represent 90% recovery of the full reflectivity. (b) Images of the oxidized (upper image) and reduced (lower image) states.

structed as shown in Figure 1, and PEDOT nanotubes were grown in 10 mM EDOT in an acetonitrile solution at 1.2 V for 40 s versus Ag/AgCl reference electrode. The device was switched from an oxidized state to a reduced state by applying alternating square potentials between 1.0 V and −1.0 V versus Ag/AgCl. The color-switching response time was measured optically from reflectivity responses at 600 nm light wavelength as a function of time at the applied potentials (Figure 5a). The de-coloring and coloring processes show switching times of 20 and 30 ms, respectively. Here, the color-switching time is defined as the time required for the system to reach 90% of its full response. Approximately, 1-[5] and 2-[4] s switching times were reported for the thin conventional film of PEDOT, although synthetically improved PEDOT derivatives showed much faster switching times (ca. 100 ms).[5] Movie film is usually played at a speed of 24 frames/s, which corresponds to switching time of 40 ms. Thus, an electrochromic device based upon PEDOT nanotubes in a PC membrane (exhibiting switching times of <40 ms) may be a good candidate for paper-like moving image displays. Figure 5b shows high color contrast and flexibility of the electrochromic device in an electrolyte solution, 100 mM $LiClO_4$ in acetonitrile. The oxidized and reduced PEDOT usually are transparent pale blue and deep blue, respectively. However, the color of the device was yellowish in the oxidized state (upper image), while it was dark blue in the reduced state (lower image) due to the sputtered gold layer. The reflective color contrast ratio between colored and de-colored states of PEDOT nanotubes was about 6, which is comparable to the previously reported values.[4,7] Due to the high flexibility of the PC template, the electrochromic device could be rolled up easily as shown in Figure 5b.

This paper is a preliminary report that a highly flexible fast electrochromic device can be fabricated based upon the PEDOT nanotubes synthesized at the low electropolymerization potential in a highly flexible PC membrane. It is worth noting that we improved the switching rate 30−50 times (20−30 ms in switching time) by using the PEDOT nanotube structure as compared to the thin film of PEDOT (∼1 s in switching time) in the flexible electrochromic device. The detailed study on the mechanism of the nanotube formation is going on by fully considering the effects of time, monomer concentration, applied potential, and others.

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Supporting Information Available: Detailed structure of the bottom electrode and electrochemical synthesis of PEDOT nanotubes in an aqueous solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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