

## Fast Electrochemistry of Conductive Polymer Nanotubes: Synthesis, Mechanism, and Application

SEUNG IL CHO AND SANG BOK LEE\*

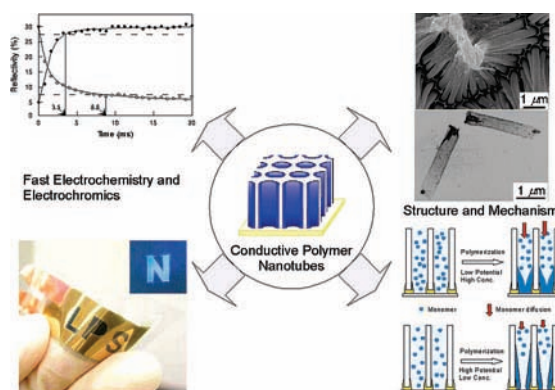
*Department of Chemistry and Biochemistry, University of Maryland,  
College Park, Maryland 20742*

RECEIVED ON SEPTEMBER 18, 2007

### CON SPECTUS

Conductive polymers exhibit several interesting and important properties, such as metallic conductivity and reversible convertibility between redox states. When the redox states have very different electrochemical and electronic properties, their interconversion gives rise to changes in the polymers' conformations, doping levels, conductivities, and colors, useful attributes if they are to be applied in displays, energy storage devices, actuators, and sensors. Unfortunately, the rate of interconversion is usually slow, at best on the order a few hundred milliseconds, because of the slow transport of counterions into the polymer layer to balance charge. This phenomenon is one of the greatest obstacles toward building rapidly responsive electrochemical devices featuring conductive polymers. One approach to enhancing the switching speed is decreasing the diffusion distance for the counterions in the polymer. We have found that nanotubular structures are good candidates for realizing rapid switching between redox states because the counterions can be readily doped throughout the thin nanotube walls. Although the synthesis of conductive polymer nanotubes can be performed using electrochemical template synthesis, the synthetic techniques and underlying mechanisms controlling the nanotube morphologies are currently not well established.

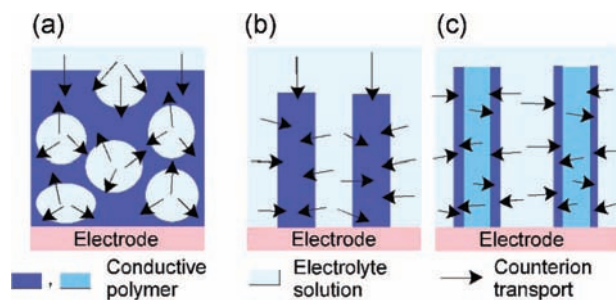
We begin this Account by discussing the mechanisms for controlling the structures from hollow nanotubes to solid nanowires. The applied potential, monomer concentration, and base electrode shape all play important roles in determining the nanotubes' morphologies. A mechanism based on the rates of monomer diffusion and reaction allows the synthesis of nanotubes at high oxidation potentials; a mechanism dictated by the base-electrode shape dominates at very low oxidation potentials. The structures of the resulting conductive polymer nanotubes, such as those of poly(3,4-ethylenedioxythiophene) (PEDOT) and polypyrrole, can be characterized using scanning electron microscopy and transmission electron microscopy. We also discuss these materials in terms of their prospective use in nanotube-based electrochemical devices. For example, we describe an electrochromic device incorporating PEDOT nanotubes that exhibits an ultrafast color switching rate ( $<10$  ms) and strong coloration. In addition, we report a supercapacitor based on PEDOT nanotubes that can provide more than 80% of its own energy density, even at power demands as high as 25 kW/kg.



### Introduction

Conductive polymers exhibit interesting and important attributes such as metallic conductivity, facile interconversion between redox states, and good tunability in their properties.<sup>1–4</sup> These characteristics are useful for an active material in

electronic or electrochemical devices and based on the dopability of the conductive polymer with counterions, photons, or charge carriers (electron–holes).<sup>1–7</sup> The doped and undoped (or redox) states have very different properties in electronic, optical, physical, chemical, and electro-



**FIGURE 1.** Schematic of facile ion transport in various nanostructures: (a) random porous structures; (b) nanowires; (c) nanotubes.

chemical aspects. Thus, the reversible interchange between the redox states in the conductive polymer gives rise to the changes in its properties including polymer conformation, doping level, conductivity, and color. These make the conductive polymer suitable for applications to displays, energy storage devices, actuators, sensors, etc.<sup>8–15</sup> However, the interchange rate is usually slow due to the rate-determining process of counterion transport into the polymer layer for charge balance.<sup>16–18</sup> It usually takes a few hundred milliseconds or more to complete the change in a regular conductive polymer film.<sup>16–18</sup> This slow interconversion rate is the main obstacle for applications of these polymer films to devices requiring fast charge/discharge capability such as electrochromics and supercapacitors.

Because the switching rate is dependent on the ion-transport rate in the polymer layer, a plausible solution to the slow interchange rate is to reduce the ion-transport resistance in the polymer. One approach is tailoring the polymer structure to introduce molecular-scale porosity.<sup>4,19,20</sup> Until now, the fastest electrochromic response achieved is ca. 90 ms, which was demonstrated in the Reynolds group for a bulky conductive polymer such as poly(dimethyl-3,4-propylenedioxythiophene).<sup>20</sup> Another molecular-structure-independent approach is to create nanoscale porosity, which is embodied in the form of nanotubes, nanowires, or random nanoporous structures.<sup>21–36</sup> These nanostructured materials can provide intrinsically high surface area leading to high charge/discharge capacities and short diffusion distances for ion transport, which leads to fast charge/discharge rates (Figure 1).<sup>23,24</sup> In particular, the nanotubular structure is attractive because its wall thickness and length can be used to control the charge/discharge rate and charge/discharge capacity, respectively. Furthermore, the inside of hollow tubes can be readily modified with other materials to further enhance their functions. In this Account, we focus on recent progress in improvement of the charge/discharge rate in conductive-polymer-based electrochemical devices by using nanotubular structures. We describe

the synthesis, growth mechanism, and characterization of dimension-controlled nanotubes and their application to fast color-switching electrochromic devices and high-power supercapacitors.

## Electrochemical Template Synthesis of Nanotubes

Conductive polymer nanotubes have been fabricated by various methods. They can be divided into three categories: template (or hard template),<sup>21,33,34</sup> pseudotemplate (or soft template),<sup>27,36</sup> and template-free methods.<sup>10,36</sup> The template method has been widely used because of its simplicity, versatility, and controllability. The hard template is usually a thin porous film of aluminum oxide or polycarbonate.<sup>34</sup> Materials have been deposited in the cylindrical pores of this film to form nanotubes or nanowires. This has been performed by methods such as pressure injection, vapor deposition, chemical deposition, and electrodeposition; and the last two of these methods are the most popular in recent research.<sup>27,33–35</sup> Here, we focus on the electrochemical template method to synthesize conductive polymer nanotubes because it enables a better control of nanotube dimension compared with the chemical method. In addition, the nanostructures produced by the electrochemical method are in solid contact with a base electrode that is beneficial for further processing steps when building an electrochemical device.

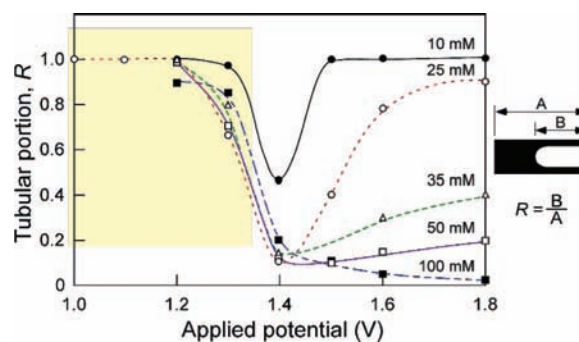
Since the first report of nanowire synthesis by Possin in 1970,<sup>29–35,37–39</sup> many metallic, inorganic, organic, and other nanowires have been made, but nanotube synthesis is more difficult and requires more delicate control of experimental parameters, such as concentration and reaction time. Only in 1990 were nanotubes first fabricated in template pores by Martin and co-workers, who called it “template synthesis.”<sup>40,41</sup> They electrochemically or chemically synthesized nanotubes and nanofibers of conductive polymers<sup>22,29,40,42</sup> such as polypyrroles, polythiophenes, and polyaniline, as well as metals<sup>41</sup> and inorganic compounds.<sup>30,31</sup> Martin and co-workers have shown that polypyrrole nanofibers (ca. 200 nm in diameters) have higher charge transport rates than a conventional film under the same conditions.<sup>29</sup> Furthermore, they also demonstrated rate capabilities of nanowires of other inorganic materials in battery applications that surpassed those of films.<sup>30,31</sup> Later on, Demoustier-Champagne and co-workers chemically and electrochemically synthesized nanotubes and nanowires of various conductive polymers such as polyaniline, polypyrrole, and poly(3,4-ethylenedioxythiophene) (PEDOT).<sup>43–46</sup> Joo and co-workers have also electrochemically synthesized the partially filled, long (up to 40  $\mu\text{m}$ ) nanotubes of conductive

polymers (polyaniline, polypyrrole, and PEDOT) by controlling polymerization time and current for potential applications to nanotip emitters for field emission displays and polymer-based transistors.<sup>47,48</sup> Recently, we have fabricated conductive polymer nanotubes with diverse inner morphologies (from hollow nanotubes to solid nanowires) to develop fast color-switching electrochromic devices.<sup>49–52</sup>

## Growth Mechanism of Conductive Polymer Nanotubes

Martin's group proposed a mechanism based on electrostatic and solvophobic interactions between the nascent polymer and pore wall to explain the nanotube growth in template pores.<sup>34</sup> These interactions induce the polymer to nucleate and grow preferentially along the pore wall to form tubular structures. As polymerization proceeds further, the polymer grows inwardly to form nanowires. This mechanism has been successfully applied not only to chemical deposition but also to the electrochemical synthesis of metallic nanotubes on pore walls modified with organocyanides or organoamines, which induce a strong affinity between metal ions and the pore wall surface.<sup>53,54</sup> However, it is insufficient to explain all the phenomena and questions arising from the electrochemical deposition (e.g., the production of partially filled nanotubes).<sup>49–52</sup> Demoustier-Champagne and co-workers considered the effect of the limited monomer and electrolyte diffusion on the growth of polypyrrole nanotubes using a pulsed chronoamperometry technique but could not find its significant effect due to the limited experimental conditions and data analyses.<sup>43</sup> Interestingly, contrary to what was observed in the synthesis of PEDOT nanotubes, they found that the interactions between pore wall and polymers were not noticeable in the synthesis of PEDOT nanotubes.<sup>44</sup> Meanwhile, some other groups have reported that the metallic nanotubes were synthesized in the template pores without modification of the wall surface.<sup>55,56</sup> All these indicate that the interaction between the pore wall and the polymer is not the sole mechanism that contributes to the nanotube formation.

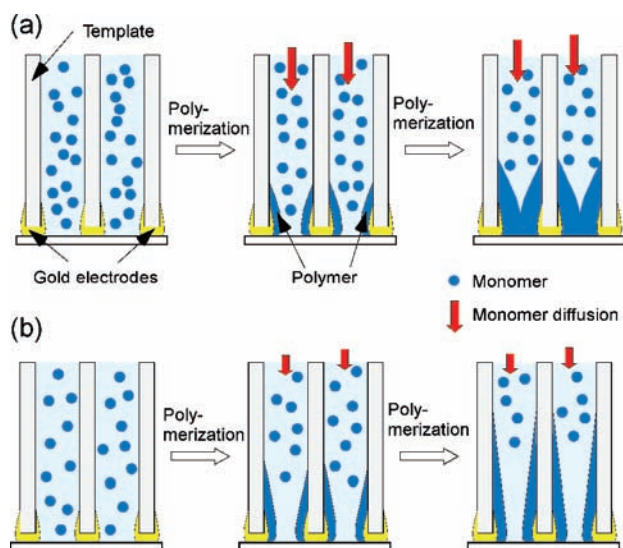
The applied potential and monomer concentration should be considered for a better understanding of electrochemical template synthesis because they are important experimental parameters in the electrodeposition. To figure out their effects, we used 3,4-ethylenedioxythiophene (EDOT) as a model compound and analyzed inner morphologies of PEDOT nanostructures synthesized at various monomer concentrations (10–100 mM) and applied potentials (1.0–1.8 V). Electropolymerization was performed potentiostatically with a Pt counter electrode and a Ag/AgCl reference electrode using 0.1



**FIGURE 2.** Potential dependence of the tubular portions as a function of applied potential at given monomer concentrations in the electrochemical template synthesis of PEDOT nanostructures. The nanotubular structures become relatively insensitive to monomer concentrations at very low oxidation potentials in the yellow boxed region.

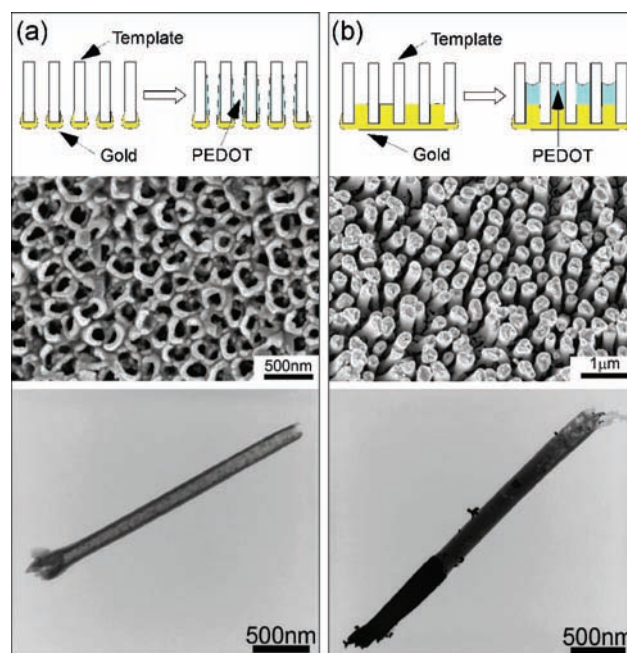
M LiClO<sub>4</sub> in acetonitrile as an electrolyte solution. The results are summarized in Figure 2 by plotting the tubular portion ( $R$ ) as a function of applied potential at given monomer concentrations. Here, the  $R$  is defined as the length of tubular section divided by total length. The potential dependence of the tubular portions has a complicated form but can be readily understood by separately considering two regions divided at 1.4 V.

**Growth Mechanism of Nanotubes at High Oxidation Potentials ( $\geq 1.4$  V).** The tubular portions increase along with the applied potentials and against monomer concentrations at the potentials higher than 1.4 V. This occurs when the reaction is limited by the diffusion of monomers. To deepen our understanding, we consider two extreme cases (Figure 3). One is the case for low potential and high monomer concentration (e.g., 1.4 V, 100 mM EDOT). Because the monomers have enough time to diffuse into the pore bottom under the slow reaction rate, the polymerization reaction occurs on the whole electrode surface without notable preference. This leads to rigid, dense nanowires. The other is for high potential and low monomer concentration (e.g., 1.8 V, 10 mM EDOT). In this situation, the polymerization reaction is very fast, and monomer supply is not sufficient to fill out the pores. The diffused monomers are immediately consumed to elongate the polymer chain. Because the reaction initiates along the electrode surface at the pore bottom, as shown in Figure 3b, the conductive polymers are continuously deposited along the pore wall. This produces long, porous, thin-walled nanotubes. Other parameters, such as electrolyte concentration, pore diameter, template thickness, stirring, temperature, also have influence on the inner morphology of nanotubes.<sup>51</sup>

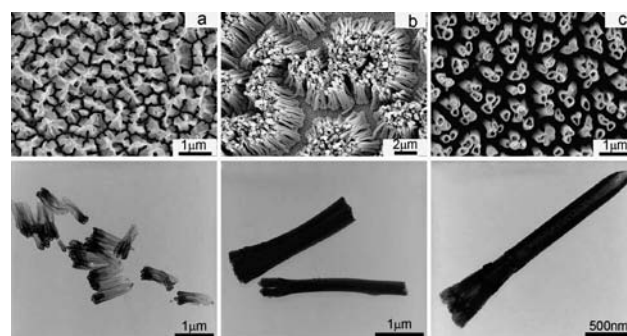


**FIGURE 3.** Growth mechanism of PEDOT nanostructures based on diffusion and reaction kinetics for high oxidation potential ( $\geq 1.4$  V). Two extreme cases are considered: (a) slow reaction rate under sufficient monomer supply and (b) fast reaction rate under insufficient monomer supply.

**Growth Mechanism of Nanotubes at Very Low Oxidation Potentials ( $< 1.4$  V).** Nanotubular structures are favored and are nearly independent of monomer concentrations at potentials lower than 1.4 V (Figure 2, yellow region), contrary to our expectation of obtaining more solid nanowire structures. This phenomenon cannot be explained by the above mechanism, implying that another deterministic parameter exists at very low oxidation potentials. Because the reaction occurs slowly at very low oxidation potentials, the morphology of base electrodes at the pore bottom becomes critical to initiate polymerization. Usually the base electrodes are made by sputtering or evaporating the thin metal layer onto the template surface. During this process the sputtered metal travels into the pores of the template and forms an annular electrode at the bottom of the pores (Figure 4a). The electrochemically active sites at these annular electrodes dominate more on the sharp top surface than on the smooth lateral surface because of high charge density at the sharp tips. As the reaction proceeds, the top end of the conductive polymers becomes good active sites for further elongation until a significant IR drop along the polymer is reached. This produces rigid nanotubes due to the slow monomer consumption and enough monomer supply at the sharp tips. This explanation is supported by the experiments on flat-top electrodes, which are generated by further depositing gold electrochemically on the annular base electrode (Figure 4b). The synthesis of PEDOT on the flat-top electrodes at the very low oxidation potential of 1.2 V gives solid nanowires. Furthermore, the potential dependence of nanotubular portions at the



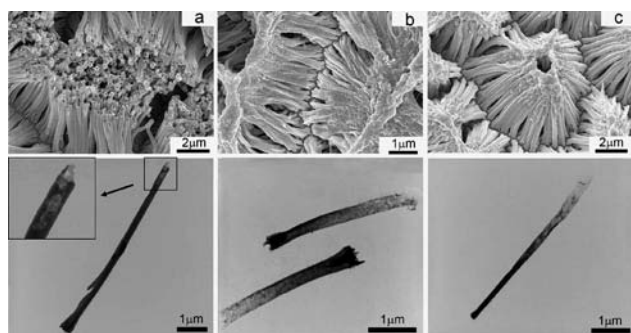
**FIGURE 4.** Growth mechanism of PEDOT nanostructures at very low oxidation potentials ( $< 1.4$  V): the predominance of electrochemically active sites on sharp electrode edges. Two base electrodes are considered: (a) annular and (b) flat-top electrodes. SEM images present the base electrode morphologies, and TEM images show the PEDOT nanostructures synthesized at the corresponding base electrodes.



**FIGURE 5.** SEM and corresponding TEM images of polypyrrole nanostructures synthesized at (a) low, (b) middle, and (c) high potentials (0.7, 1.4, and 1.8 V, respectively).

flat-top electrodes becomes explainable by the diffusion and reaction kinetics seen in the high oxidation potential region ( $\geq 1.4$  V) in Figure 2, which shows that the tubular portion increases with the reaction potentials. Therefore, the base electrode shape is the key factor determining nanotube morphology below 1.4 V, and EDOT polymerization preferentially occurs on the tips of the annular base electrodes.

**Other Conductive Polymers.** The elaborated growth mechanism of PEDOT nanotubes is also useful to the nanotube synthesis of other conductive polymers such as polypyrrole and poly(3-hexylthiophene). Figure 5 shows the electron microscopy images of the polypyrrole nanostructures synthe-



**FIGURE 6.** SEM and corresponding TEM images of three representative PEDOT nanostructures: (a) nanowires with an open-ended tip, (b) hollow nanotubes, and (c) partially filled nanotubes.

sized at three different conditions: low, middle, and high potentials (0.7, 1.4, and 1.8 V, respectively). As in PEDOT synthesis, the potential dependence of nanotubular portions in polypyrrole synthesis showed a similar trend: minimum tubular portions at moderate potentials around 1.4 V (Figure 5b). The growth of the rigid polypyrrole nanotubes at very low oxidation potential of 0.7 V can be explained by the mechanism based on electrochemically active sites at the annular electrodes. On the other hand, the increase in tubular portions at the potentials above 1.4 V is understood by the mechanism based on the reaction rate and monomer diffusion. Poly(3-hexylthiophene) has also shown a similar trend (data not shown here) that can also be understood using this elaborated growth mechanism.<sup>51</sup>

### Characterization of Nanotube Structures

The scanning electron microscopy (SEM) images of conductive polymer nanotubes are quite different from those of metallic nanotubes because of the polymeric flexibility of the conductive polymers. Figure 6 shows the SEM images of three representative nanostructures of a conductive polymer (nanowire, partially filled nanotube, and hollow nanotube). The common feature in the three SEM images is the collapse and aggregation of the nanostructures due to strong surface tension between the nanostructures and the liquid during solvent evaporation in a sampling process. This phenomenon has also been observed in metallic or inorganic nanostructures. The notable difference in the SEM images of the conductive polymer nanostructures is the degree of collapse. The hollow nanotubes have highly wrinkled and collapsed structures from the bottom, rather than smooth cylindrical structures, because their walls are too thin to maintain their original structures (Figure 6b). This wrinkled and collapsed structure in the SEM image can be a useful indicator of the tubular structure in the conductive polymers. The partially filled nanotubes look like a combination of a nanotube and a nanowire (Figure 6c).

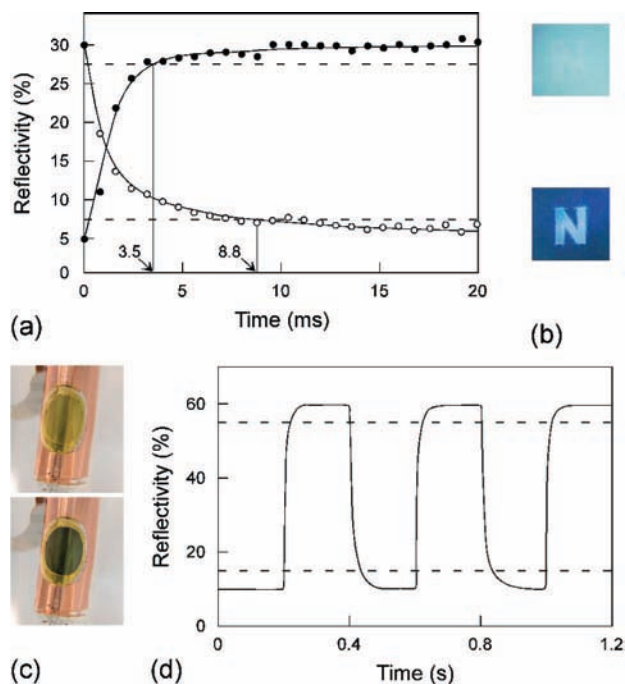
The lower part of the partially filled nanotubes resembles a cylindrical nanowire, while their upper part resembles a collapsed nanotube.

The transmission electron microscopy (TEM) images of the conductive polymer nanotubes are also interesting, as shown in the lower images in Figure 6. The outer diameters of nanotubes (ca. 300 nm) are much larger than the pore diameters of the alumina template (ca. 200 nm). This indicates that the cylindrical structure of the individual nanotube becomes flat due to its low rigidity. This feature is manifested in the partially filled nanotubes: the diameter of the tubular section continuously increases toward its top because of gradual collapse of the tubular section.

### Fast Color-Switching Electrochromic Devices

Electrochromics is one of the fascinating properties of conducting polymers. This electrochromic property can be applied to smart windows, rear-view mirrors, electronic paper, displays, stealth technology, etc.<sup>4</sup> Fast color switching is a prerequisite, especially for display applications. At a theater, movies are usually played at a speed of 24 frames/s. Thus, the color switching time should be less than 40 ms to play movies with good quality. In the case of PEDOT films, it usually takes 1–2 s to change colors.<sup>19,57</sup> Even though reduction of the film thickness can improve the color-switching rate, this is accompanied by the loss of color contrast and vividness of the thin film. Recently, we have pioneered fast electrochromics using a nanotubular structure of PEDOT and achieved extremely fast electrochromic responses without sacrificing the color contrast.<sup>49</sup> The long, thin-walled nanotubes of PEDOT can provide short diffusion pathways for counterions for fast redox switching (less than 10 ms; Figure 7a), as well as strong coloration (contrast of 6) for display applications (Figure 7b). We have also developed two additional nanotube-based electrochromic devices: flexible reflectance-type and window-type devices. A flexible, translucent, track-etched polycarbonate (PC) film was used as a template for the flexible reflectance-type device, while a transparent porous alumina film was used for the window-type device.

**Flexible Reflectance-Type Electrochromic Devices.** Figure 7c shows a fabricated flexible electrochromic device. PEDOT nanotubes are grown in 10 mM EDOT in acetonitrile at 1.2 V for 40 s. The device is switched from the oxidized to reduced states by applying alternating square potentials between 1.0 and –1.0 V. The electrochromic device shows strong coloration and flexibility. Its color is yellowish at the oxidized state due to the background of the sputtered gold

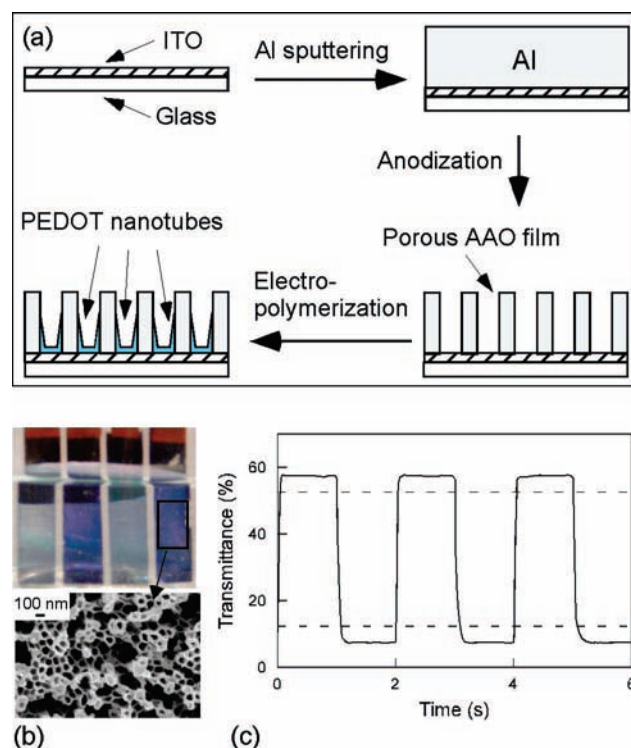


**FIGURE 7.** (a) Reflectivity plot for a nonflexible electrochromic device monitored at 600-nm wavelength for alternating potentials between  $-1.0$  and  $1.0$  V. (b) Patterned letter "N" on the PEDOT nanotube arrayed film. (c) Fabricated flexible electrochromic device at oxidized (upper image) and reduced (lower image) states. (d) Reflectivity plot for a flexible electrochromic device. The dashed lines represent 90% recovery of the full reflectivity.

electrode (upper image), while it is dark blue at the reduced state (lower image). The reflectance ratio between the colored and decolored states of the PEDOT-nanotube-based electrochromic device is about 6 (Figure 7d), which is comparable to the previously reported values.<sup>57</sup> Due to the high flexibility of the PC template, the electrochromic devices are rolled up easily. The oxidation and reduction processes show switching times of 20 and 30 ms, respectively (Figure 7d).

**Window-Type Electrochromic Devices.** The merit of porous alumina structures is that they can be prepared on various substrates such as glass, silicon, and others.<sup>58–60</sup> Indium-doped tin oxide (ITO) is a suitable substrate as a transparent electrode. Figure 8a illustrates the fabrication scheme for a window-type electrochromic device. First, a thin layer of aluminum ( $1\text{--}2\ \mu\text{m}$  thick) is sputter-coated onto ITO-coated glass. Then the resulting aluminum film is anodized at a constant voltage to generate highly ordered porous alumina structures. The pores of the alumina template are chemically widened to desired pore diameters.<sup>58–60</sup> Then, PEDOT is electrodeposited in the pores to grow nanostructures.

There are two difficulties in synthesizing conductive polymer nanotubes in this system. The first is that the base electrode shape at the pore bottom is flat rather than annular.



**FIGURE 8.** (a) Schematic diagram of the synthesis of PEDOT nanotubes in porous alumina structures on an ITO/glass substrate. (b) Electrochromic device with four windows (the first and third windows are oxidized (pale blue) while the second and fourth ones are reduced (dark blue)) and a SEM image at a certain area of one window, showing the PEDOT nanotubular array structure after the removal of the template. (c) Plot of the transmittance change at 600 nm as a function of time.

Thus, it is difficult to synthesize rigid PEDOT nanotubes at very low oxidation potential on the basis of the mechanism by the annular electrodes. We rely on the mechanism based on diffusion and reaction kinetics. The second problem is that the porous film is much thinner ( $\sim 2\ \mu\text{m}$ ) than the commercial one ( $\sim 60\ \mu\text{m}$ ). This situation makes the monomer diffusion into the pores much easier. Thus, the synthesis of PEDOT nanotubes at the flat base electrodes in the thin template pores is performed at lower monomer concentration and higher applied potential (2.5 mM EDOT and 1.8 V).

Figure 8b shows an electrochromic device with four windows composed of PEDOT nanotube array. The oxidized (first and third) and reduced (second and fourth) windows of the PEDOT nanotube array exhibit transparent pale blue and deep blue, respectively. The color-switching times for decoloring (oxidation) and coloring (reduction) processes are 50 and 70 ms, respectively. These response speeds are a bit slower than those in our previous results (4–30 ms).<sup>49,50</sup> This can be explained by the slow diffusion of counterions to the partially filled nanotubes. Meanwhile, the window-type electrochromic device shows good transmit-

tance of about 56%, which is comparable to the value (ca. 54%) reported in a conventional film.<sup>57</sup> This good transmittance can be attributed to the glass-like transparency of the alumina template/ITO/glass substrate.

## High-Power Energy Storage Devices: Supercapacitor

Another interesting application of conductive polymer nanotubes using their fast charge/discharge characteristic is high-power energy storage devices such as supercapacitors and batteries.<sup>61–64</sup> Recent batteries can provide high energy densities but still suffer from low power densities. One approach to this problem is the use of nanostructured batteries, which can provide high power density by enhancing the charge/discharge rates.<sup>30,31</sup> Another approach is to use supercapacitors, which produce necessarily high peak power in conjunction with a battery.<sup>64</sup>

The conductive polymers can store energy by accumulating/releasing countercharges under the electric field arising from their redox reactions.<sup>13,64</sup> Even though the redox-type supercapacitors made of conductive polymers can provide high specific capacitances, the power capability is not satisfactory due to the slow ion-transport processes during the redox reaction of the polymer. This can be overcome by using nanotubular structures as in the fast electrochromic devices.

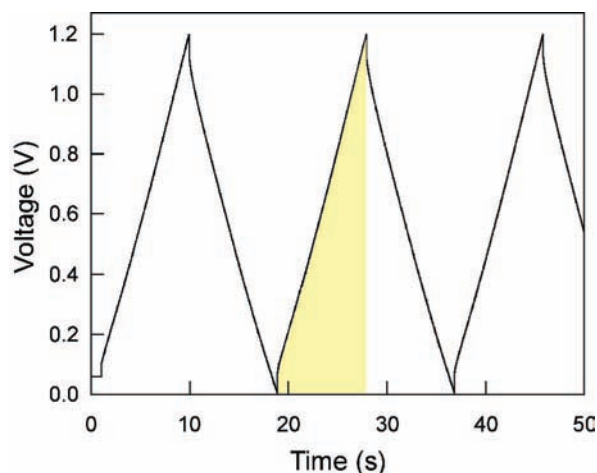
The energy ( $E$ ) of any energy storage device under a constant current is given by

$$E = \int V dq = I \int V dt \quad (1)$$

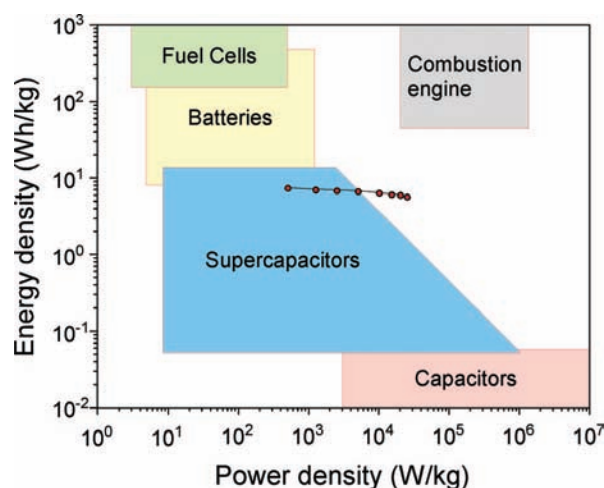
where  $V$ ,  $q$ ,  $I$ , and  $t$  represent voltage, charge, current, and time, respectively. The energy of a capacitor is usually obtained from a  $V-t$  curve under a constant current. This is done in electrochemistry by using the charge/discharge cycling at a constant current density. Figure 9 shows the galvanostatic charge/discharge cycling curve at the current density of 5 mA/cm<sup>2</sup> for a PEDOT-nanotube-based electrode (500 mC/cm<sup>2</sup> in polymerization charge density). The specific capacitance ( $C_s$ ) is given by

$$C_s = I/(m_e dV/dt) \quad (2)$$

where  $m_e$  is the weight of the electrode material (0.3 mg/cm<sup>2</sup>). The obtained specific capacitance is about 132 F/g. The high linearity and symmetry (or uniform slope) in the charge/discharge curve of the nanotube-based electrode represents its closeness to an ideal capacitor. The slower the voltage change, the larger the energy is because the stored energy is the area under a  $V-t$  graph. The obtained energy density is about 27



**FIGURE 9.** Galvanostatic charge/discharge curve of a PEDOT-nanotube-based electrode at the current density of 5 mA/cm<sup>2</sup>. The shaded area multiplied by current represents the total energy.



**FIGURE 10.** Plot of energy densities versus power densities (Ragone plot) for various energy storage devices. Closed circles represent data from the PEDOT-nanotube-based supercapacitor. Data for other systems are adapted from ref 61.

W · h/kg. Meanwhile, the power ( $P$ ) is defined as the energy generated or consumed in a time interval  $dt$

$$P = dE/dt = VI \quad (3)$$

Because the voltage changes linearly with time, the average power density becomes half of the maximum power density and is about 10.5 kW/kg at this condition.

The high power performance of a symmetric supercapacitor based on PEDOT nanotubes is exhibited in a Ragone plot (Figure 10),<sup>62,63</sup> which is a plot of energy density versus power density obtained at various current densities (0.5, 1, 2.5, 5, 10, 15, 20, and 25 mA/cm<sup>2</sup>). In many electrochemical supercapacitors, the available energy density is significantly reduced at the power density higher than 10 kW/kg. However, the PEDOT-nanotube-based supercapacitor can maintain at least

80% of its maximum energy density (ca. 7.5 W·h/kg) even when the power density is boosted to 25 kW/kg. Therefore, the nanotubular structure is a good candidate for a supercapacitor that provides high power density without significant loss of its energy density.

## Conclusion and Outlook

In this Account, we introduced the prospect of nanotubular structures to achieve fast charge/discharge rates in conductive polymers and presented our work related to the controlled synthesis, growth mechanism, and characterization of PEDOT nanotubes in electrochemical template synthesis. The morphology of nanostructures electrochemically grown in the template pores was predicted by considering the diffusion and reaction kinetics as well as the interaction between pore wall and polymers at high oxidation potentials. However, the base electrode shape plays an important role in determining nanotube morphology at very low oxidation potentials. This elaborated mechanism is applicable to other conductive polymers and inorganic materials and helpful for fabrication of composite structures such as nanotube/nanotube, nanotube/nanowire, or nanotube/nanoparticles, as well. The controlled synthetic technique for nanotubular structures made it feasible to investigate the performances of nanotube-based electrochemical devices. The electrochromic device of PEDOT nanotubes showed ultrafast color switching rate and strong coloration; the supercapacitor of PEDOT nanotubes provided its own energy density at high power demand. However, our research is still in its infancy with respect to realistic devices. For example, we need to improve the color vividness and multiplicity in the electrochromic devices and specific capacitance and energy density in the supercapacitor. Recently, we have found that nanotube-based composite structures of conductive polymer and metal oxide have enhanced electrochemical properties and have been investigating further exciting developments concerning electrochemical devices. Our understanding on the growth mechanism of conductive polymer nanotubes and synthetic techniques to control the nanotube morphology will be a cornerstone to fabricate diverse nanostructures and accomplish faster, more efficient electrochemical devices.

*This work has been supported by the Laboratory for Physical Sciences, LG Chem., the National Institute of Standards and Technology, the UMD-NSF-MRSEC under grant DMR 05-20471, SEF (shared experimental facility), and the University of Maryland.*

## BIOGRAPHICAL INFORMATION

**Seung Il Cho** received his B.S. (1992), M.S. (1994), and Ph.D. (2001) in Chemistry from the Seoul National University, Korea. He was a visiting research fellow at Brigham and Women's Hospital (affiliate of Harvard Medical School) in Massachusetts and a postdoctoral research associate in Electrical Engineering and Computer Science and Nano Bioelectronics & Systems Research Center at the Seoul National University. He is currently a postdoctoral research associate in the Department of Chemistry and Biochemistry at the University of Maryland. His research interests include synthesis, characterization, and application of nanomaterials.

**Sang Bok Lee** received his B.S. (1990), M.S. (1992), and Ph.D. (1997) in Chemistry from the Seoul National University, Korea. After finishing his Ph.D., he worked at a DRAM maker, LG Semicon (Hynix), for two years as a senior research engineer and held a postdoctoral position at the University of Florida, before joining the Department of Chemistry and Biochemistry, University of Maryland (UMD), College Park, MD, in 2002. His research focuses on the synthesis and control of nanotube structures with various materials and the applications of the nanotubes from biomedicine to electronic devices.

## FOOTNOTES

\* Corresponding author. E-mail: slee@umd.edu.

## REFERENCES

- Heeger, A. J. Semiconducting and metallic polymers: The fourth generation of polymeric materials. *J. Phys. Chem. B* **2001**, *105*, 8475–8491.
- Bredas, J. L.; Street, G. B. Polarons, bipolarons, and solitons in conducting polymers. *Acc. Chem. Res.* **1985**, *18*, 309–315.
- McCullough, R. D. The chemistry of conducting polythiophenes. *Adv. Mater.* **1998**, *10*, 93–116.
- Groenendaal, L. B.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. Poly(3,4-ethylenedioxythiophene) and its derivatives: Past, present and future. *Adv. Mater.* **2000**, *12*, 481–494.
- Sirringhaus, H.; Tessler, N.; Friend, R. H. Integrated optoelectronic devices based on conjugated polymers. *Science* **1998**, *280*, 1741–1744.
- Gunes, S.; Neugebauer, H.; Sariciftci, N. S. Conjugated polymer-based organic solar cells. *Chem. Rev.* **2007**, *107*, 1324–1338.
- Argun, A. A.; Aubert, P.-H.; Thompson, B. C.; Schwendeman, I.; Gaupp, C. L.; Hwang, J.; Pinto, N. J.; Tanner, D. B.; MacDiarmid, A. G.; Reynolds, J. R. Multi-colored electrochromism in polymers: Structures and devices. *Chem. Mater.* **2004**, *16*, 4401–4412.
- Berdichevsky, Y.; Lo, Y.-H. Polypyrrole nanowire actuators. *Adv. Mater.* **2006**, *18*, 122–125.
- Imisides, M. D.; John, R.; Wallace, G. G. Microsensors based on conducting polymers. *CHEMTECH* **1996**, *19*, 25.
- Huang, J.; Virji, S.; Weiller, B. H.; Kaner, R. B. Nanostructured polyaniline sensors. *Chem.—Eur. J.* **2004**, *10*, 1314–1319.
- Chien, J. C. W.; Schlenoff, J. B. Limiting battery performance parameters for polyacetylene. *Nature* **1984**, *311*, 362–363.
- Carlberg, J. C.; Inganas, O. Poly(3,4-ethylenedioxythiophene) as electrode material in electrochemical capacitors. *J. Electrochem. Soc.* **1997**, *144*, L61–L64.
- Arbizzani, C.; Mastragostino, M.; Meneghello, L. Polymer-based redox supercapacitors: A comparative study. *Electrochim. Acta* **1996**, *41*, 21–26.
- Kros, A.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. Conducting polymers with confined dimensions: Track-etch membranes for amperometric biosensor applications. *Adv. Mater.* **2002**, *14*, 1779–1782.
- Rajesh, B.; Thampai, K. R.; Bonard, J.-M.; Mathieu, H. J.; Xanthopoulos, N.; Viswanathan, B. Conducting polymeric nanotubules as high performance methanol oxidation catalyst support. *Chem. Commun.* **2003**, 2022–2023.



- 16 Foot, P. J. S.; Mohammed, F.; Calvert, P. D.; Billingham, N. C. Diffusion in conducting polymers. *J. Phys. D: Appl. Phys.* **1987**, *20*, 1354–1360.
- 17 Genies, E. M.; Bidan, G.; Diaz, A. F. Spectroelectrochemical study of polypyrrole films. *J. Electroanal. Chem.* **1983**, *149*, 101–113.
- 18 Penner, R. M.; Van Dyke, L. S.; Martin, C. R. Electrochemical evaluation of charge-transport rates in polypyrrole. *J. Phys. Chem.* **1988**, *92*, 5274–5282.
- 19 Groenendaal, L.; Zotti, G.; Aubert, P.-H.; Waybright, S. M.; Reynolds, J. R. Electrochemistry of poly(3,4-alkylenedioxythiophene) derivatives. *Adv. Mater.* **2003**, *15*, 855–879.
- 20 Cirpan, A.; Argun, A. A.; Grenier, C. R. G.; Reeves, B. D.; Reynolds, J. R. Electrochromic devices based on soluble and processable dioxothiophene polymers. *J. Mater. Chem.* **2003**, *13*, 2422–2428.
- 21 Martin, C. R. Template synthesis of electronically conductive polymer nanostructures. *Acc. Chem. Res.* **1995**, *28*, 61–68.
- 22 Penner, R. M.; Martin, C. R. Controlling the morphology of electronically conductive polymers. *J. Electrochem. Soc.* **1986**, *133*, 2206–2207.
- 23 Arico, A. S.; Bruce, P.; Scrosati, B.; Tarascon, J.-M.; van Schalkwijk, W. Nanostructured materials for advanced energy conversion and storage devices. *Nat. Mater.* **2005**, *4*, 366–377.
- 24 Long, J. W.; Dunn, B.; Rolison, D. R.; White, H. S. Three-dimensional battery architectures. *Chem. Rev.* **2004**, *104*, 4463–4492.
- 25 Ghosh, S.; Inganäs, O. Conducting polymer hydrogels as 3D electrodes: Applications for supercapacitors. *Adv. Mater.* **1999**, *11*, 1214–1218.
- 26 Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. One-dimensional nanostructures: Synthesis, characterization, and applications. *Adv. Mater.* **2003**, *15*, 353–389.
- 27 Jang, J. Conducting polymer nanomaterials and their applications. *Adv. Polym. Sci.* **2006**, *199*, 189–259.
- 28 Kaneto, K.; Maxfield, M.; Nairns, D. P.; MacDiarmid, A. G.; Heeger, A. J. Electrochemistry of polyacetylene, (CH)<sub>x</sub>, characteristics of polyacetylene cathodes. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 3417–3429.
- 29 Van Dyke, L. S.; Martin, C. R. Electrochemical investigations of electronically conductive polymers. 4. Controlling the supermolecular structure allows charge transport rates to be enhanced. *Langmuir* **1990**, *6*, 1118–1123.
- 30 Patrissi, C. J.; Martin, C. R. Sol-gel-based template synthesis and Li-insertion rate performance of nanostructured vanadium pentoxide. *J. Electrochem. Soc.* **1999**, *146*, 3176–3180.
- 31 Li, N.; Martin, C. R.; Scrosati, B. A high-rate, high-capacity, nanostructured tin oxide electrode for lithium-ion battery applications. *Electrochem. Solid-State Lett.* **2000**, *3*, 316–318.
- 32 Kolmakova, A.; Moskovits, M. Chemical sensing and catalysis by one-dimensional metal-oxide nanostructures. *Annu. Rev. Mater. Res.* **2004**, *34*, 151–180.
- 33 Kline, T. R.; Tian, M.; Wang, J.; Sen, A.; Chan, M. W. H.; Mallouk, T. E. Template-grown metal nanowires. *Inorg. Chem.* **2006**, *45*, 7555–7565.
- 34 Martin, C. R. Nanomaterials—a membrane-based synthetic approach. *Science* **1994**, *266*, 1961–1966.
- 35 Huber, C. A.; Huber, T. E.; Sadoqi, M.; Lubin, J. A.; Manalis, S.; Prater, C. B. Nanowire array composites. *Science* **1994**, *263*, 800–802.
- 36 Zhang, D.; Wang, Y. Synthesis and applications of one-dimensional nano-structured polyaniline: An overview. *Mater. Sci. Eng., B* **2006**, *134*, 9–19.
- 37 Possin, G. E. A method for forming very small diameter wires. *Rev. Sci. Instrum.* **1970**, *41*, 772–774.
- 38 Pontifex, G. H.; Zhang, P.; Wang, Z.; Haslett, T. L.; AlMawlawi, D.; Moskovits, M. STM imaging of the surface of small metal particles formed in anodic oxide pores. *J. Phys. Chem.* **1991**, *95*, 9989–9993.
- 39 Whitney, T. M.; Jiang, J. S.; Seanson, P. C.; Chien, C. L. Fabrication and magnetic properties of arrays of metallic nanowires. *Science* **1993**, *261*, 1316–1319.
- 40 Martin, C. R.; Van Dyke, L. S.; Cai, Z.; Liang, W. Template synthesis of organic microtubules. *J. Am. Chem. Soc.* **1990**, *112*, 8976–8977.
- 41 Martin, C. R. Template synthesis of polymeric and metal microtubules. *Adv. Mater.* **1991**, *3*, 457–459.
- 42 Parthasarathy, R. V.; Martin, C. R. Template-synthesized polyaniline microtubules. *Chem. Mater.* **1994**, *6*, 1627–1632.
- 43 Demoustier-Champagne, S.; Ferain, E.; Jerome, C.; Jerome, R.; Legras, R. Electrochemically synthesized polypyrrole nanotubules: effects of different experimental conditions. *Eur. Polym. J.* **1998**, *34*, 1767–1774.
- 44 Demoustier-Champagne, S.; Stavaux, P.-Y. Effect of electrolyte concentration and nature on the morphology and the electrical properties of electropolymerized polypyrrole nanotubules. *Chem. Mater.* **1999**, *11*, 829–834.
- 45 Duvail, J. L.; Retho, P.; Garreau, S.; Louarn, G.; Godon, C.; Demoustier-Champagne, S. Transport and vibrational properties of poly(3,4-ethylenedioxythiophene) nanofibers. *Synth. Met.* **2002**, *131*, 123–128.
- 46 Delvaux, M.; Duchet, J.; Stavaux, P.-Y.; Legras, R.; Demoustier-Champagne, S. Chemical and electrochemical synthesis of polyaniline micro and nanotubules. *Synth. Met.* **2000**, *113*, 275–280.
- 47 Kim, B. H.; Park, D. H.; Joo, J.; Yu, S. G.; Lee, S. H. Synthesis, characteristics, and field emission of doped and de-doped polypyrrole, polyaniline, poly(3,4-ethylenedioxythiophene) nanotubes and nanowires. *Synth. Met.* **2005**, *150*, 279–284.
- 48 Joo, J.; Kim, B. H.; Park, D. H.; Kim, S. H.; Seo, D. S.; Shim, J. H.; Lee, S. J.; Ryu, K. S.; Kim, K.; Jin, J.-I.; Lee, T. J.; Lee, C. J. Fabrication and applications of conducting polymer nanotube, nanowires, nanohole, and double wall nanotube. *Synth. Met.* **2005**, *153*, 313–316.
- 49 Cho, S. I.; Kwon, W. J.; Choi, S. J.; Kim, P.; Park, S. A.; Kim, J.; Son, S. J.; Xiao, R.; Kim, S. H.; Lee, S. B. Nanotube-based ultrafast electrochromic display. *Adv. Mater.* **2005**, *17*, 171–175.
- 50 Cho, S. I.; Choi, D. H.; Kim, S.-H.; Lee, S. B. Electrochemical synthesis and fast electrochromics of poly(3,4-ethylenedioxythiophene) nanotubes in flexible substrate. *Chem. Mater.* **2005**, *17*, 4564–4566.
- 51 Xiao, R.; Cho, S. I.; Liu, R.; Lee, S. B. Controlled electrochemical synthesis of conductive polymer nanotube structures. *J. Am. Chem. Soc.* **2007**, *129*, 4483–4489.
- 52 Cho, S. I.; Xiao, R.; Lee, S. B. Electrochemical synthesis of poly(3,4-ethylenedioxythiophene) nanotubes toward a fast window-type electrochromic device. *Nanotechnology* **2007**, *18*, 405705.
- 53 Brumlik, C. J.; Martin, C. R. Template synthesis of metal microtubules. *J. Am. Chem. Soc.* **1991**, *113*, 3174–3175.
- 54 Bao, J.; Tie, C.; Xu, Z.; Zhou, Q.; Shen, D.; Ma, Q. Template synthesis of an array of nickel nanotubules and its magnetic behavior. *Adv. Mater.* **2001**, *13*, 1631–1633.
- 55 Yoo, W.-C.; Lee, J.-K. Field-dependent growth patterns of metals electroplated in nanoporous alumina membranes. *Adv. Mater.* **2004**, *16*, 1097–1101.
- 56 Zhao, Y.; Guo, Y.-G.; Zhang, Y.-L.; Jiao, K. Fabrication and characterization of highly ordered Pt nanotubule arrays. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1766–1768.
- 57 Kumar, A.; Welsh, D. M.; Morvant, M. C.; Abboud, K.; Reynolds, J. R. Conducting poly(3,4-alkylenedioxythiophene) derivatives as fast electrochromics with high contrast ratios. *Chem. Mater.* **1998**, *10*, 896–902.
- 58 Crouse, D.; Lo, Y.-H.; Miller, A. E.; Crouse, M. Self-ordered pore structure of anodized aluminum on silicon and pattern transfer. *Appl. Phys. Lett.* **2000**, *76*, 49–51.
- 59 Masuda, H.; Yasui, K.; Sakamoto, Y.; Nakao, M.; Tamamura, T.; Nishio, K. Ideally ordered anodic porous alumina mask prepared by imprinting of vacuum-evaporated Al on Si. *Jpn. J. Appl. Phys. Part 2* **2001**, *40*, L1267–L1269.
- 60 Chu, S. Z.; Wada, K.; Inoue, S.; Todoroki, S. Formation and microstructures of anodic alumina films from aluminum sputtered on glass substrate. *J. Electrochem. Soc.* **2002**, *149*, B321–B327.
- 61 Winter, M.; Brodd, R. J. What are batteries, fuel cells, and supercapacitors? *Chem. Rev.* **2004**, *104*, 4245–4269.
- 62 Pell, W. G.; Conway, B. E. Quantitative modeling of factors determining Ragone plots for batteries and electrochemical capacitors. *J. Power Sources* **1996**, *63*, 255–266.
- 63 Conway, B. E.; Birss, V.; Wojtowicz, J. The role and utilization of pseudocapacitance for energy storage by supercapacitors. *J. Power Sources* **1997**, *66*, 1–14.
- 64 Pushparaj, V. L.; Shajumon, M. M.; Kumar, A.; Murugesan, S.; Ci, L.; Vajtai, R.; Linhardt, R. J.; Nalamasu, O.; Ajayan, P. M. Flexible energy storage devices based on nanocomposite paper. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 13574–13577.