Fabrication of Conducting Polymer Nanowires

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1. Introduction

The advancement of nanotechnology provides opportunities for fabrication of nanoscale materials and higher performance devices using nanomaterials with high precision. Currently, various nanomaterials and nanostructures in the range of 1 to 100 nm have been produced by chemical and physical methods. Among various nanostructured materials, one-dimensional (1D) materials, such as nanowires, nanotubes, nanorods, and nanobelts, have potential applications in nanoscale electronics (Cui & Lieber, 2001), optoelectronics (Duan et al., 2001), photonics (Gudiksen et al., 2002; Huang et al., 2001), sensors (Cui et al., 2001), and solar cells (Law et al., 2005) due to their unique electrical, chemical, and optical properties (Li et al., 2006; Thelander et al., 2006; Wang et al., 2008). Nanowires are useful in chemical or biological sensors for detecting single molecules because they have a high surface-to-volume ratio and a highly sensitive 1D nanostructure that gives rise to large conductivity change associated with binding molecules (Cui et al., 2001; Ramanathan et al., 2005).

Conducting polymers, such as polypyrrole, polyaniline, polythiophene, and their derivatives, are promising materials for synthesis of nanostructured materials and devices (Langea et al., 2008; Malinauskas et al., 2005). Compared with other materials, conducting polymers have some unique electrical, chemical, and optical properties because of their conjugated structures, and they are easily synthesized using chemical or electrochemical synthetic methods at room temperatures with low cost (Aleshin, 2006; Briseno et al., 2008; Guimard et al., 2007; Xia et al., 2010). Conducting polymers have electrical and optical properties similar to those of metals and semiconductors, while maintaining the flexibility and properties commonly associated with conventional polymer substances (Dai et al., 2002; Heeger, 2002; Shirakawa, 2002). For example, the electrical conductivity of these polymers can be adjusted from an insulator to traditional metals by varying the species and concentrations of doping ions. Undoped conducting polymers with conductivities of $10^{-10}$ to $10^{-5}$ S cm$^{-1}$ can be changed into semiconducting or metallic materials with conductivities of 1 to $10^4$ S cm$^{-1}$ through a chemical or electrochemical doping process (MacDiarmid, 2002). Also, optical absorption bands and mechanical volume of conducting polymers can be changed by entrapped doping ions. Therefore, they have been used for various applications such as electronic devices (Hashizume, 2006), optoelectronic devices (Noy et al., 2002), actuators (Berdichevsky & Lo, 2006), transistors (Alam et al., 2005), and chemical sensors (Bangar et al., 2009; Garcia-Aljaro et al., 2010).

In recent years, 1D conducting polymer nanostructures have been demonstrated to have improved performance with low dimensionality. Many different fabrication methods have
been applied to making conducting polymer nanowires. These methods include e-beam lithography, focused ion-beam etching, dip-pen lithography, electro-spinning, DNA scaffolding, mechanical break junction, hydrodynamically focused stream, and nanopore template. In this chapter, we will introduce various fabrication methods for conducting polymer nanowires. This chapter is describes four methods: the template method, electro-spinning method, nanolithography method, and microfluidic method.

2. Template method

The template method has been widely used to fabricate 1D conducting polymer nanostructures such as nanowires and nanotubes because of its simplicity, versatility, and controllability (Cho & Lee, 2007; Tran et al., 2009). Generally, the template method has been classified into a hard-template method, which uses a nanopore film such as anodic aluminium oxide (AAO), and a soft-template method, which uses the self-assembly ability of molecules such as surfactants and DNA.

2.1 Hard template

In the early 1990s, Martin and co-workers introduced the fabrication of various conducting polymer nanowires such as polypyrrole, polyaniline, poly(3-methylthiophene), and polyacetylene using a nanoporous polycarbonate and aluminium oxide template. Figure 1 shows SEM images of these nanowires and their templates (Cai et al., 1991; Cai & Martin, 1989; Liang & Martin, 1990; Martin et al., 1993; Parthasarathy & Martin, 1994). These polymers are electrochemically or chemically polymerized from corresponding monomers using an oxidizing agent (Martin, 1994). This process is composed of simple steps: 1) fill nanopores of the membrane with monomers, 2) polymerize the monomers inside the nanopores, and 3) remove the nanopore template to obtain pure polymers (Tran et al., 2009).

Fig. 1. Conducting polymer nanowires and template from early research by Martin and co-workers. SEM images of (a) polycarbonate and (b) the AAO template (Martin, 1994) and of (c) polyaniline (Partharathy & Martin, 1994) and (d) polyacetylene nanowires (Liang & Martin, 1990).
Later, a method was sought to control the composition or properties of conducting polymer nanowires. Jèrôm et al. (1999) fabricated high-aspect-ratio polypyrrole nanowires 600 nm in diameter and 300 μm in length using a two-step electrochemical method. After electropolymerization of polyacrylate films on the cathode, polypyrrole was synthesized by chronopotentiometry under a constant current of 0.5 mA/cm² in a dimethylformamide solution. Fu et al. (2001) synthesized polythiophene nanowires on flexible gold film by electro-polymerization of thiophene in boron trifluoride diethyl etherate solution using an alumina membrane. The length and diameter of various conducting polymer nanowires synthesized using AAO templates can be controlled by polymerization time and current (Joo et al., 2005; 2003; Park et al., 2005; Xiao et al., 2007). The electrical properties of conducting polymers were controlled through various synthetic conditions, such as doping level, dopant, and template-dissolving solvents (Kim et al., 2005). Li et al. (2001; 2002) copolymerized pyrrole/aniline and pyrrole/thiophene composite nanowires using AAO. The diameter and length could be controlled by the shape of the nanopores of the AAO membrane. The composition of nanowires can be controlled by electrochemical polymerization potentials, and it can be estimated indirectly using cyclic voltammetry and IR spectroscopy. Wang et al. (2005) fabricated polypyrrole/carbon nanotube composite nanowires to improve the electrical and mechanical properties of polymers. Electropolymerization of polypyrrole was achieved using carboxylated CNT (carbon-nanotube) dopants in nanoporous alumina membranes. Figure 2 shows a SEM image of various conducting polymer nanowires using a hard template.

![SEM Images of various conducting polymer nanowires](https://www.intechopen.com)
The fabrication method using a hard template provides a straightforward system to synthesize conducting polymer nanowires. The diameter and length of nanowires are controllable by adjusting the pore size, thickness of the membrane, and polymerization conditions. On the other hand, this method requires a post-synthesis task to obtain pure polymer nanowires. In some cases, polymer nanowires can be destroyed or damaged because the template removal process entails harsh conditions. AAO, one of the most widely used nano templates, is a representative example.

2.2 Soft template

The soft-template method which is also called the self-assembly method typically uses surfactants or DNA as templates. This method has the advantage of a simple fabrication process, and the template removal process is achieved under mild conditions or is not required. Thus, it is possible to avoid the damage that occurs during the removal of a hard template.

Surfactants offer a representative soft template because of their self-assembly ability. Wan et al. (1998) accidentally discovered that polyaniline nanowires could be synthesized by \textit{in-situ} doping polymerization in the presence of $\beta$-naphthalene sulfonic acid ($\beta$-NSA) as the dopant without the need to use any membrane as a hard template. This method does not require the removal of a $\beta$-NSA template after polymerization because the membrane is a dopant of polyaniline. Wei et al. (2002) reported that the diameter of polyaniline nanowires can be controlled by adjusting the ratio of $\beta$-NSA to aniline monomer concentration. Zhang et al. (2004; 2006) reported various polypyrrole nanostructures in the presence of various surfactants (anionic, cationic, or non-ionic surfactants) with various oxidizing agents. Various polypyrrole nanostructures can be synthesized according to the selection of surfactants and oxidizing agents. Especially, it is possible to obtain nanowire structures in the presence of long-chain cationic surfactants, such as cetyltrimethylammonium bromide, dodecyltrimethylammonium bromide, and anions of the oxidizing agent of ammonium persulfate. Li & Zhang et al. (2004) reported dendritic polyaniline nanowires with diameters between 60 and 90 nm by chemical oxidative polymerization in the presence of a special surfactant gel, which consisted of hexadecyltrimethylammonium chloride ($\text{C}_{16}\text{TMA}$), acetic acid, aniline, and water at -7°C. Figure 3 shows examples of conducting polymer nanowires fabricated using surfactant as a template.

Fig. 3. SEM Images of conducting polymer nanowires using surfactant as a template; (a) polypyrrole nanowires (Zhang et al., 2006); (b) dendric polyaniline nanowires (Li & Zhang, 2004).
DNA molecules also provide attractive soft templates for nanowire fabrication because they are chemically robust and are able to react with monomers without obvious structural requirements or functional group adjacency (Moon et al., 2010; Xia et al., 2010). Ma et al. (2004) immobilized stretched double stranded λ-DNA on a thermally oxidized silicon chip using the molecular combining method. The DNA templates were incubated in aniline monomer solutions (19 mM, pH = 4.0), and the phosphate groups in the DNA templates and protonated aniline monomers were organized by electrostatic interactions. The aligned aniline monomers were enzymatically polymerized by adding horseradish peroxidase and \( \text{H}_2\text{O}_2 \) successively. Figure 4 shows the fabrication process of polyaniline/DNA nanowires introduced by Ma et al. (2004). Polypyrrole nanowires were chemically polymerized on mica with FeCl\(_3\) oxidant using DNA as a template by Dong et al. (2007). Moon et al. (2010) also chemically polymerized polypyrrole nanowires using DNA as a template on a (3-aminopropyl)triethoxysilane modified silicon wafer with ammonium persulfate as an oxidant. Hassanien et al. (2010) reported that polyindole nanowires were synthesized on a λ-DNA template by chemical oxidation of indole using FeCl\(_3\) as an oxidant. Figure 3 shows AFM images of conducting polymer nanowires using DNA as a template.

![Fabrication of a polyaniline nanowire immobilized on a Si surface with stretched double stranded DNA as a guiding template (Ma et al., 2004).](image1)

![AFM images of DNA/conducting polymer nanowires; (a) DNA/polypyrrole nanowire. The highlighted part is a DNA/polypyrrole nanowire and the others are bare DNA-scaffold molecules (Dong et al., 2007); (b) DNA/polypyrrole nanowire (Moon et al., 2010); (c) DNA/polyindole nanowires aligned between Au electrodes (Hassanien et al., 2010).](image2)
3. Electro-spinning

Electro-spinning has been recognized as one of the most efficient techniques for the fabrication of micro- or nanoscale polymer fibers. Electro-spinning occurs with the development of a jet when the repulsion forces of a charged solution overcome the surface tension of the solution under a high electrostatic field. When the jet solidifies, polymer nanofibers remain (Huang et al., 2003; Reneker & Chun, 1996). In recent years, it has been reported that various polymers including conducting polymers have been successfully electrospun into polymer nanofibers. MacDiarmid et al. (2001) reported fabrication of polyanilin nanowires with sub-100 nm diameters doped with d,l camphorsulfonic acid (PAn.HCSA) as a blend in polyethylene oxide (PEO) based on their previous research (Norris et al., 2000). Zhou et al. (2003) reported an electrospun polyaniline/polyethylene oxide blend nanowire with diameters below 30 nm with optimized process parameters. Chronakis et al. (2006) reported electrospun polypyrrole/PEO nanofibers with diameters in the rage of about 70–300 nm with improved electrical conductivity using the functional doping agent di(2-ethylhexyl) sulfosuccinate sodium salt (NaDEHS). Ju et al. (2007) reported an electro-spinning method for polypyrrrole/sulfonated-poly(styrene-ethylene-butylene-styrene) composite nanofibers with an average diameter of about 300 nm and a uniform and smooth appearance. Choi et al. (2010) reported a method of fabricating electrospun poly(3,4-ethylenedioxythiophene) (PEDOT): poly(styrenesulfonate) (PSS)/PVP nanofibers for a chemical vapor sensor, and Laforgue & Robitaille (2010) introduced a method for fabrication of PEDOT nanofibers by a combination of electro-spinning and vapor-phase polymerization. Figure 6 shows SEM images of conducting polymer nanowires fabricated using electro-spinning.

![SEM Image](image_url)

Fig. 6. SEM Image of (a) polyaniline fibers with an average diameter of 139 nm, (MacDiarmid et al., 2001), (b) polypyrrole/PEO composite nanofibers (the scale bar is 1 μm), (Chronakis et al. 2006), (c) PEDOT:PSS/PVP nanofibers (Choi et al., 2010), and (d) PEDOT nanofibers fabricated using a combination of electro-spinning and vapor-phase polymerization (the scale bar is 5 μm) (Laforgue & Robitaille, 2010).
Electro-spinnning is a very effective method for fabrication of conducting polymer nanowires; however, it is limited in its application for various electronic devices owing to the nonwoven fiber shape and the difficulty of controlling positioning. Kameoka et al. (2003) presented a method for the controlled deposition of oriented nanowires with the rotation of collectors using a chopper motor. Although this method is not limited by nonwoven shape, it still has limits compared with other methods.

4. Nanolithography

Nanowire sensors are among the most promising applications because of their impressive sensitivities to detect nanomolar concentrations of DNA (Kemp et al., 2007) and ~10 fM concentrations of micro-RNAs (Fan et al., 2007). To detect such small concentrations of analytes, electrode–wire–electrode assemblies are required (Thapa et al., 2009). The aforementioned fabrication methods can yield uniform nanowires with a high throughput, but they require the elaborate post-synthesis task of positioning the nanowires with the desired precision and electrical contact properties to create one-dimensional nanostructures. The simplest nanowire-positioning technique uses dielectrophoresis (Dan et al., 2007) and self-assembly at the air/water interface (Xu et al., 2009). On the other hand, nanolithography makes it possible to synthesize the nanowires in the desired position. This method allows simultaneous synthesis and positioning of the conducting polymer nanowires.

4.1 Dip-pen nanolithography

Dip-pen nanolithography (DPN), in which an atomic force microscope (AFM) tip transfers alkane thiol to a gold surface, is one of the best-known nanolithography techniques. It is possible to directly write on the desired position without a photomask using an AFM tip as a "pen" (Piner et al., 1999). Lim & Mirkin (2002) synthesized conducting polymer nanowires using DPN using self-doped sulfonated polyaniline (SPAN) and doped polypyrrole as "ink" on a positively charged surface using 2% (trimethoxysilyl)propyldiethylenetriamine (DETA) (Fig. 7). Because SPAN and doped polypyrrole are negatively charged, an electrostatic interaction occurs between the negatively charged polymer and the positively charged substrate, leading to the alignment of the polymer chains along the substrate surface. The aligned polymer chains then form nanowires upon drying.

![Fig. 7. Schematic representation of dip-pen nanolithography for charged conducting polymers (Lim & Mirkin, 2002).](www.intechopen.com)
interaction makes it possible to draw conducting polymer nanowires using DPN. It is possible to control the width of the polymer pattern owing to the linear dependence on the root of contact time (Fig. 8). Maynor et al. (2002) reported the PEDOT line deposition on an anodic silicon surface simultaneous with oxidation. Fig. 9 shows conducting polymer lines drawn using DPN.

![Fig. 8](image8.png)

Fig. 8. Diffusion properties of conducting polymers on modified silicon substrates. Lateral force microscopy (LFM) images of (a) SPAN dots and (b) polypyrrole dots as a function of tip-substrate contact time. (c) Plot of the feature radius as a function of $t^{1/2}$ for SPAN and (d) polypyrrole (Lim & Mirkin, 2002).

![Fig. 9](image9.png)

Fig. 9. (a) LFM (left) and topography (right-top) images of polypyrrole lines and the cross-sectional profile (right-bottom) (Lim & Mirkin, 2002). (b) PEDOT line patterned on SiO$_2$. Polymer line width: 200 nm; scale bar: 1 μm (Maynor et al., 2002).

4.2 e-beam lithography
Yun et al. (2004) and Ramanathan et al. (2004) reported a method of fabricating an array of individually addressable conducting polymer nanowires using e-beam lithography. Figure 10 shows schematic diagram and SEM image of a conducting polymer nanowire using e-
beam lithography. They patterned nano channel arrays for the electro-deposition of wires between the electrodes using e-beam lithography. Monomer solutions, such as pyrrole (0.06 M in 0.01 M KCl) or aniline (0.1 M in 0.01 M KCl), were placed on the nanochannel between the electrodes, and the electro-polymerization was generated by applying an electric current. Because the electro-polymerization occurs only in nanochannels, it is possible to control various properties of the nanowires such as dimensions, position, alignment, and chemical composition. This technique is similar to the hard-template method in that nanowire synthesis occurs in nanochannels. The hard-template method is suitable for fabricating nanowires with high density within definite area, whereas e-beam lithography is suitable for fabricating a single nanowire at a desired position, such as in an electrode–wire–electrode structure.

Conducting-polymer fabrication methods based on nanolithography such as Dip-pen and e-beam are attractive because it is possible to synthesize conducting polymers in a desired position to avoid the post-synthesis positioning task. However, they have obvious limitations, such as high cost and low yield, which are characteristic of nanolithography.

Fig. 10. (a) Schematics diagram of a structure used for the electrochemical wire growth (Yun et al., 2004) and (b) SEM image of a 100 nm width and 4 \( \mu \)m length polyaniline nanowire (Ramanathan et al., 2004).

5. Fabrication using microfluidics

Nanolithography is an attractive technique because nanowires with a diameter of several tens of nanometers can be reproducibly obtained at a desired position. However, nanolithography is not suitable for commercialization because of a low yield and high cost. Fabrication methods using microfluidics make it possible not only to synthesize nanowires in the desired position but also to produce nanowires at a low cost. Limitations such as reproducibility and a slightly larger diameter of nanowires still exist.

5.1 Hydrodynamic focusing

Hou et al. (2008) introduced a fabrication method that uses the characteristics of laminar flow in micro-channels. In the microfluidic system, a low Reynolds number causes a small diffusion layer between miscible liquids. The microfluidic device reported by Hou et al. was made up of polydimethylsiloxane micro-channels and a platinum electrode array on a glass substrate (Fig. 11a). The pyrrole solution (0.1 M pyrrole, 0.1 M LiClO, and 1.0 mM HCl) was inserted into the centre of the microchannel at a constant flow rate, while the distilled water
comprised a sheath flow at a variable flow rate. Figure 11b shows the fluorescence images of hydrodynamically focused pyrrole solutions containing a fluorescent component (10 nM 5-carboxyfluorescein). The two-step sheath flow created a compressed monomer layer in the centre of the microchannel, and this layer flowed across the platinum electrode arrays. The thickness of the compressed layer was controlled by changing the flow rate of the sheath flow. Applying constant current between the electrodes, a conducting polymer micropattern was electropolymerized in a focused monomer stream as a dynamic template (Fig. 11c). The width of the polypyrrole wire could be controlled by the width of the focused stream, the gap between electrodes, and the electro-polymerization time.

Fig. 11. (a) Microfluidic device for a hydrodynamically focused laminar stream. (b) Fluorescence images of hydrodynamically focused streams with various widths in a microfluidic device. (c) SEM images of various widths of polypyrrole; 5-, 2-, and 1-μm width (Hou et al., 2008).

Strictly speaking, it is hard produce a nanowire because the smallest published width of a conducting polymer wire is just 1 μm. However, this technique shows the potential to fabricate conducting polymer nanowires by controlling the polymerization conditions. Moreover, the conducting polymer can be synthesized with low cost and high throughput by applying an electric field to the desired electrodes. For this reason, we introduce a hydrodynamic focused fabrication method in this chapter.

5.2 Dielectrophoresis
Choi et al. (2009) electrochemically synthesized CNT-conducting polymer nanowires using dielectrophoresis. CNTs and monomer precursors were gathered between the electrodes where the electric-field gradient is greater due to their higher conductivity compared with the surrounding medium (Fig. 12a). After the suspension was partially removed, the remaining suspension was compressed, and it formed a concave meniscus with evaporation due to surface tension (Fig. 12b). As a result, the electric current was concentrated through the compressed CNTs and monomers. Gathered CNTs generated dynamic templates for electro-polymerization of conducting polymer nanowires. Because nanowires are synthesized between the electrodes to which an electric field is applied, it is possible to individually address a conducting polymer nanowire array to a single chip. Figures 13 shows SEM images of various conducting polymer nanowires on a single chip. These CNT-
conducting polymer nanowires are a few hundred nanometers in diameter and a few micrometers in length.

Fig. 12. Microscope images of the CNT–conducting polymer nanowire fabrication process using dielectrophoresis. (a) Attraction of the CNT and monomer molecules between electrodes with an AC electric field; (b) Compression of the CNT and monomer by suspension evaporation; (c) A CNT–conducting polymer nanowire synthesized between electrodes.

Fig. 13. SEM images of a CNT–conducting polymer composite nanowire array on a single chip. (a) polypyrrole nanowire; (b) polyaniline nanowire; (c) polythiophene nanowire (Choi et al., 2009).

6. Conclusion

This chapter has provided a brief overview of the methods of fabricating conducting polymer nanowires. Since Martin and co-workers first reported conducting polymer nanowires, which were synthesized using nanopore templates, various fabrication methods
have been developed. Template methods consist of a simple synthesis process to produce nanowires and can control the size of nanowires by adjusting the nanopore of templates. Electro-spinning is a method to obtain a mass quantity of nanowires with a nonwoven fiber structure using a high electric field. Template and electro-spinning methods are possible options to fabricate nanowires with high yield and low cost; however, they require a post-synthesis task to address the desired nanowire position in some applications that need a single nanowire. In the case of nanolithography, wire synthesis and positioning occur simultaneously because polymerization occurs according to the nano pattern drawn by e-beam or dip-pen nanolithography. This method can control the properties of each individual nanowire; however, it is expensive, and a long production time is required to synthesize a large quantity of nanowires. In the case of the method using microfluidics, polymerization occurs in compressed monomer precursors through hydrodynamic focusing or dielectrophoresis. This method allows for the control of the properties of each individual nanowire in a similar manner to nanolithography. Compared with nanolithography, microfluidics has advantages such as low cost and high yield along with limitations such as size control and reproducibility. Although many techniques have been developed to fabricate conducting polymer nanowires, still some limitations remain such as size control, low yield, high cost, or long production time due to post-synthesis tasks. Further research is needed to overcome these limitations and develop applications for commercialization.

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8. References


This potentially unique work offers various approaches on the implementation of nanowires. As it is widely known, nanotechnology presents the control of matter at the nanoscale and nanodimensions within few nanometers, whereas this exclusive phenomenon enables us to determine novel applications. This book presents an overview of recent and current nanowire application and implementation research worldwide. We examine methods of nanowire synthesis, types of materials used, and applications associated with nanowire research. Wide surveys of global activities in nanowire research are presented, as well.

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