Synthesis of Microwires of Polypyrrole via Chemical Polymerization using Track Etch Membrane as Template

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Received 5 March 2014; published online 14 June 2014

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Abstract

Low dimensional structures of conducting polymers, particularly polypyrrole, have attracted a great attention of researchers and engineers in recent years because of their diverse potential application on account of their unique properties of large aspect ratio, good electrical conductivity, environmental stability and biocompatibility. The present work describes synthesis of polypyrrole microwires by template assisted chemical polymerization at room temperature using FeCl₃ as an oxidant. In this technique, the track etch membrane used as a template was fitted between two chambers in a chemical cell in such a way that the template acts as a separating wall between the chambers. One chamber was filled with an aqueous monomer pyrrole solution and other was filled with oxidant reagent of ferric chloride. Chemical polymerization takes place within the pores of the template as the monomer and the oxidant reagent diffuse towards each other, react to yield the conductive polymer which grows as microstructure in the shape of pores of host template. Synthesized samples have been characterized by Scanning Electron Microscopy (SEM), which reveals that the morphology of the microwires matches with the morphology of pores as mould in host template. Diameter, orientation and direction of growth of microwires were almost uniform because of the confined growth of microwires in the ordered and symmetric pores of TEM template. Conductivity of polypyrrole microwires was estimated equal 20.152 S/m form current-voltage characteristics measured using a two-probe-method.

Keywords: Conductive polymer; Track Etch Membrane (TEM); Polypyrrole (PPy); Nanowires; Template; Chemical polymerization

1. Introduction

In the recent years, conductive polymers have attracted a great attention because of their excellent chemical and physical properties originating from their unique p-conjugated system and switchable conductivity between insulator and metal (Yang et al., 2007). Conducting polymers have promising...
potential applications in optics, electronics, sensors, artificial muscles and biodiagnostics, electro catalysts, electroluminescent materials, gas separating membranes, anticorrosive coatings, electromagnetic shields, energy storage devices, microlithography and electrophotography. (Wanekaya et al., 2006; Yun et al., 2005; Thapa et al., 2009; Yang et al., 2007; Pan et al., 2011; Wei, 2010; Berdichevsky and Lo, 2005; Vernitskaya and Efimov, 1997). Among conducting polymers, polypyrrole (PPy) has fascinated wide interest because of its relative ease of synthesis and availability of the initial monomers. As a consequence of good conductivity, redox properties, environmental stability and biocompatibility; PPy has attractive applications like drug delivery, gas separation, glucose sensors, ammonia sensors and many more (Massafera et al., 2009; Eisazadeh, 2007; Kumar et al., 2011; Ansari, 2006).

Bulk quantities of PPy can be obtained as fine powders using the oxidative polymerization of the monomer by selected transition metal ions in water or various other solvents and its conductivity depends on the conditions and reagents used in the oxidation (Ansari, 2006) Synthesis of low dimensional structures of conducting polymers is an emerging subfield of the polymeric electronics arena (Thapa et al., 2009). Major advances have been made in the synthesis and characterization of versatile nanostructure materials for diverse applications. PPy with low dimensional structures such as nanowires, nanotubes or nanosprings, are one of the most prominent candidates in nanoscience and nanotechnology; and have their application in fabrication of high density nanoscale devices. In biosensor applications, biomolecules can be recognized by immobilizing or trapping them into the nano/micro structures which modulate the resistance of the electrode-wire-target and signal generated due to change in resistance evidence that particular biomolecule (Kumar et al., 2011; Thapa et al., 2009; Kros et al., 2005). To enable the interfacing of diagnostic instrumentation with the wire or target, synthesis of polymeric wires with predicted morphology, orientation and directional growth (Thapa et al., 2009) are of considerable interest. Conducting polymers have also been used as materials for artificial muscles which expand or contract upon application of an electric field or a pH change (Otero and Sansiñena, 1995; Baughman, 1996). PPy is also potential vehicle for drug delivery and its matrix serves as a container for proteins (Geetha et al., 2006). In forthcoming research trends, PPy is being investigated for new possible applications – as artificial muscle fibers to be used in devices to mimic as biological nano and microactuators (Berdichevsky and Lo, 2005), in low temperature fuel cell technology to enhance the catalyst dispersion in the carbon support layers (Unni et al., 2010), to sensitize cathode electrocatalysts (Olsan et al., 2010) and for sensing applications using the chemiresistor principle (Chakraborty and Luo, 2009). PPy coated glass fiber fabrics have also been used to develop a salisbury screen absorber and possess characteristics for their probable exploitation as radar absorbing materials (Marchant et al., 1998; Eisazadeh, 2007). Recently, Zhou et al. (2013) has reported that a water-resistant polyurethane sponge coated with a thin layer of polypyrrole has been developed and it is capable to absorb 20 times its weight in oil and is reusable.

The sensitivity of electrical properties of PPy to radiation, temperature, gases and stress leads to diverse areas of investigation. However, applications have been limited due to its lack of processability, flexibility and strength. These limitations have motivated the present work to hunt facile technique for the synthesis and assembly of reproducible aligned nano/micro scale structures of PPy with predictable and determined dimensions in flexible substrate which possess the mechanical properties of substrate retaining the electrical properties of conducting polymers. Template based synthesis technique of micro/nanostructures is versatile and of significant interest
as they give up reproducible wire shapes, lengths and directional growth, according to the morphology of molds in host material (Chakarvarti and Vetter, 1998). PPy nano/micro structures can be prepared by both electrochemical and chemical approaches in various organic solvents and in aqueous solution using hard template guided synthesis within the channels, holes, cavities or related nanosized structural units of the template (Kumar, et al., 2004; Yang et al., 2007). After synthesis, post-synthesis treatment is required to wipe out the host template material in order to get the final product as micro/nanostructures of conductive polymers. Porous anodic alumina oxide, track-etched membranes, and mica are the three types of templates generally used for template based synthesis. With the advances in new applications, it is required that the morphology of low dimensional structures can precisely be synthesized by altering the shape and size of the host template. For this, track etch membrane (TEM) is a good alternative to be used as a template (Kumar and Chakarvarti, 2006; Enculescu, 2006; Chakarvarti, 2009) because of their distinctive properties, which are controllable such as - optical transparency, smooth surface, pore size, pore density, shape, inertness, thinness, high mechanical strength, toughness, low diffusion rate that gives the membrane a unique overall performance (Chakarvarti, 2009). These membranes are formed by exposing the polymer sheet or some other insulating material with heavy ion particles resulting in the formation of latent tracks in the material which are subsequently etched by hydrofluoric acid to form pores. The size and shape of pores in TEM are readily controllable which depends on the nature of incident ions, detector material and etching conditions. The shape of the pores can be tailored cylindrical, conical, double conical and funnel-like under controlled etching conditions. Density and orientation of pores depend on the collimation of ion beam during irradiation process (Ferain and Legras, 2001; Apel, 2001; Apel, et al., 2001; Karim et al., 2009; Garg et al., 2012; Quinn et al., 1972). The development of controlled and predictable pores in TEMs has already been achieved in research to supply accurate membranes apt to the template assisted synthesis of geometrically known micro/nanostructures.

In the present work, microwires of PPy were chemically synthesized using template based technique in which pores of polycarbonate TEM are used as moulds. This technique is simple, easy, economical, and yields reproducible array of ordered microwires of determined morphology with directional growth within pores. The TEM impregnated with PPy microwires have a flexible surface with the retained mechanical strength of polycarbonate membrane, making it suitable for potential applications based on chemiresistor principle which is the motivation behind this work. The morphological characterization of PPy microwires has been carried out using scanning electron microscopy (SEM). These microwires have uniform diameter, length, alignment and directional growth, which correspond to the morphology of pores of TEM acting as moulds. The conductivity of these PPy microwires has been estimated using the I-V characteristics.

2. Experimental Details

2.1. Materials
Samples of polycarbonate (monomer composition C_{16}H_{14}O_{3}, trade name Makrofol, Bayer, clear film of thickness 20 μm) were irradiated with 13.02 MeV/n Xe (fluence 10^6 ions/m²) utilizing the heavy ion accelerator UNILAC facility at GSI, Darmstadt, Germany. The charged-particle bombardment (or irradiation) on PC film results in the formation of damaged areas (latent tracks) on the film which are subsequently chemically etched by dipping the irradiated sample in 6N NaOH solution at 50°C for 20 minutes resulting into the formation of discrete cylindrical pores with a defined pore
size (Kumar, et al., 2004; Kumar and Chakarvarti, 2006). Their pore diameter increases almost linearly with time of chemical etching. This porous Polycarbonate TEM was used as template for the chemical synthesis of PPy microwires. Pyrrole and ferric chloride were used for chemical polymerization which were procured from Molychem, Mumbai, India of GR grade. Double distilled water was used to prepare the aqueous solutions. Dichloromethane was used for post treatment to dissolve polycarbonate matrix followed by washing with ethanol to obtain PPy microwires.

2.2 Method
The PCTEM sample was fitted between two chambers of chemical cell in such a way that it acts as dividing wall (Kumar, et al. 2004) and template for chemical synthesis as shown in the Fig. 1. The O rings were placed on the both sides of the template at the aperture of the chambers for sealing, so that solutions do not spill out or leak from the chambers. Then one chamber was filled with an aqueous PPy solution of 0.5 M concentration and other chamber was filled with 0.5 M solution of oxidant reagent of ferric chloride with the help of syringe through openings on the upper side of the cell. The monomer and the oxidant reagent diffuse with in pore towards each other and react to yield the conductive polymer and start to grow as in the shape of pores in PCTEM template. The cell was placed for 12 hours at room temperature of about 25°C to continue the polymerization process. After 12 hours the cell was opened, the deposition of brownish colour was seen on template in the area of aperture which indicated that PPy microwires were formed within the pores of PCTEM. The sample was rinsed with double distilled water and dried.

2.3 Characterization
Morphological characterization of the PPy microwires was carried out using scanning electron microscopy (SEM). The cleaned and dried samples were mounted on the specially designed aluminum stubs with the help of double sided adhesive tape. The matrix of polycarbonate host material was dissolved by pouring the dichloromethane drop by drop for about 20 minutes on the sample and after that the sample is again dried and coated with a layer of gold using JEOL, Fine Sputter JFC-1100 sputter coater. Images were viewed and recorded under JEOL, JSM 6100 scanning electron microscope at an accelerating voltage of 15KV. Figs. 2-4 show scanning electron micrographs of PPy microwires from different views.
The current-voltage characteristics were measured and drawn by stepping voltage between -10 to 10 V using Keithley 2400 Series Source Measurement Unit by two-probe-method. The membrane was held on the copper surface acting as one electrode and contact on the other side of membrane template was made with needle copper electrode having well defined cross sectional area. Silver paste was used to ensure good contact of electrodes. The electrical conductivity of the single PPy microwires formed within the pores of TEM template is calculated by measuring the bulk resistance of microwires in area of needle electrode.

3. Results and Discussions

Synthesis of PPy via chemical polymerization process entails oxidative polymerization of pyrrole monomer by chemical oxidants in aqueous solvent in order to bring out polypyrrole as fine powders of blackish brown colour. Ferric chloride and water are established best oxidant and solvent for chemical polymerization of pyrrole (Eisazadeh, 2007; Vernitskaya and Efimov, 1997; Ansari, 2006). The monomer and the oxidant reagent filled in the separate chambers diffuse towards each other and react within pores of template to produce the conductive polymer. The mechanism of formation of PPy microwires via template method from aqueous solutions in two chambers of a cell may be understood as follows:

\[
\begin{align*}
n\ C_4H_4NH + 2\ FeCl_3 & \rightarrow (C_4H_2NH)_n + 2\ FeCl_2 + 2\ HCl \\
(C_4H_2NH)_n + x\ FeCl_3 & \rightarrow (C_4H_2NH)_nCl_x + x\ FeCl_2
\end{align*}
\]

Polymerization takes place through the formation of the pi-radical cation \( C_4H_4NH^+ \). This electrophile attacks the C-2 carbon of an un-oxidized molecule of pyrrole to give out a dimeric radical \( [C_4H_2NH]_2^+ \) and this process replicates itself many times. Conductive forms of PPy are prepared by oxidation (“p-doping”) of the polymer. The cell is left for adequate time of 12 hours, the above process continues till the pores are completely filled with the PPy resulting into the formation of microwires. The blackish brown colour was seen on TEM Template with in the area of aperture of the O rings, when the cell was opened, which is the indication of the formation of PPy. By repetitions of experiment, it has been observed that factors such as reaction temperature, time, nature of oxidant and concentration of oxidizing agent affect the polymerization process, and finally conductivity of polymer. The polycarbonate TEM impregnated with PPy microwires is observed as flexible, smooth and rugged surface which leads to it as potential substrate for holding biomolecules in biosensing and biomedical applications, as these materials are biocompatible.

Fig. 2-4 illustrates the SEM micrographs of free standing released PPy microwires from the template that look like thin solid cylindrical wires. SEM photographs also witness that shape and size of microwires are high quality replica of voids in TEM template. Morphology, alignment and orientation of synthesized PPy microwires are quite uniform as they grow homogeneously via chemical polymerization within confined ordered and symmetric pores of host TEM template. The corresponding diameter and length of pores and synthesized microwires are similar for the reason that embedded pores within TEM template act as excellent moulds (Chakarvarti and Vetter, 1998; Enculescu, 2006; Chakarvarti, 2009).
Fig. 2. SEM Image of PPy Microwires from top view

Fig. 3. SEM Image of PPy Microwires from side view

Fig. 4. SEM Image of PPy Microwires from closer view
As far as the segment to segment and wire to wire variation is concerned, the same is understood to be negligible in conjunction with least variation of morphology and alignment of pores achieved by controlling homogeneity of the incident ion beam, target material and etching conditions while preparing the TEMs which is a well established distinct feature of ion track etch technique (Apel, 2001; Ferain and Legras, 2001; Nikezic and Yu, 2004; Sartowska et al., 2012; Kumar and Chakarvarti, 2006). The standard deviation is significantly small due to narrow pore size distribution that is a function of pore density nearly equal to flux density of irradiated ion beam which is $10^6$ ions/m$^2$ in the present work. The average diameter and length of synthesized PPy microwires, measured by SEM analysis, are found 1.6 um and 20 um respectively.

**Fig. 5.** Schematic to Take I-V Curve of Parallel Microwires Covered Under Electrode Cross Section

Electrical conductivity of conductive polymer is one of the most important properties for analytical diverse applications. The electrical conductivity of synthesized PPy microwires at individual wire level cannot be measured directly due to constraints of laboratory facilities to hold single microwire and also due to certain cross sectional area of the electrodes used in two probe method to measure the conductivity. But one can derive indirectly the electrical conductivity of single microwire by measuring the bulk resistance of composite membranes, having microwires embedded in pores of TEM, for the cross sectional area of the needle electrode. Fig. 5 illustrates the schematic to draw the I-V curve for the measurement of bulk resistance of the number of parallel microwires covered under the cross section of electrode. The current-voltage characteristics were measured and drawn by stepping voltage between -10 to 10 V using Keithley 2400 Series Source Measurement Unit. Fig. 6 shows the symmetric bidirectional Ohmic behavior of the synthesized PPy microwires. There is some lag (non-linearity) in I-V plot at the small voltage level which may be attributed to the well known fact that when an electrolyte solution is filled in a nanopore and an
electrical potential gradient is imposed between the two ends of the pore, an ionic current will be established. If the nanopore is predominantly tapered, with one end narrower than the other, however, the absolute value of the ionic current varies with the sense of the potential gradient. In other words, the ionic current shows a preferred direction. This ionic-current rectification phenomenon is usually visualized more by asymmetric diode-like current–voltage ($I$–$V$). However, in our case the pores are not perfectly conical, but a similar effect of the lower magnitude is observed. In the inset the $I$-$V$ curve at small $V$ has been included in Fig. 6 of the $I$-$V$ plot; if the initial behavior points are excluded then $I$-$V$ plot seems linear even at small $V$.

**Fig. 6.** $I$-$V$ Characteristics of PPy Microwires

Polycarbonate matrix in host template is non-conducting and does not contribute in conductivity. Hence, bulk resistance $R$ can be expressed as effective parallel resistance of the microwires deposited with in pores in the electrode cross section area $A$ (Kumar et al., 2004; Garg et al., 2012) and can be written as:

$$\frac{1}{\bar{R}} = \frac{n}{\bar{R}'}$$

(1)

where, $\bar{R}$ is the resistance offered by single microwire,

$n$ is the number of microwires in the area of electrode $A$ which is equal to:

$$n = N \times A,$$

(2)
where, N is the density of pores in TEM which is assumed equal to density of irradiated heavy ions on the template membrane.

Therefore, equation (1) can be rewritten as:

\[
\frac{1}{R} = \frac{NA}{\hat{R}} ,
\]

the \(\hat{R}\) resistance offered by the single PPy microwire formed in the pore of TEM template having length \(\ell\) equal to thickness of the template and cross sectional area \(\hat{\ell}\) equal to pore area can be given as:

\[
\hat{R} = \rho \frac{\ell}{\hat{\ell}} = \rho \left( \frac{\ell}{\pi r^2} \right) ,
\]

where, \(\rho\) is the specific resistance of PPy and \(r\) is the radius of the microwire,

from above equation conductivity \(k\) can be expressed as:

\[
k = \frac{1}{\rho} = \frac{\ell}{\pi r^2 \hat{R}} ,
\]

substituting the value of \(\hat{R}\) from equation (3) to equation (5),

\[
k = \frac{1}{\rho} = \frac{\ell}{\pi r^2 RNA}
\]

The bulk resistance of PPy wires in area \(A\), electrode cross-sectional area, was estimated by the I-V plot in Fig. 6, which comes out 31034.55717 ohms. The density of pores \(N\) is equal to influence density of irradiated heavy ions \((10^6\) ions/m\(^2\)) and the length of the wires is 20 um equal to thickness of the TEM. The measured average diameter of the PPy microwires is about 1.6 um. The electrical conductivity of PPy microwires, in the present work, is calculated using the equation (6) and is found 20.152 S/m which indicates good conductivity in case of this conductive polymer. The estimated conductivity of synthesized microwires agrees with the previously reported conductivity values of 50±30 S/m for PPy nano wires (Thapa et al., 2009; Shiratori et al., 1998).

As per earlier studies (Vernitskaya and Efimov, 1997; Ansari, 2006), the oxidative doping creates polarons and bipolarons resulting conduction in PPy as a consequence of which the mechanism of charge transport along segments of the conjugated polymer chains as well as hopping of these charges from chain to chain take place. Electrically conducting polymers are semiconductor with a filled valence band and an empty conduction band, separated by an energy band gap. The oxidative doping of PPy creates new bipolarons bands in the energy gap, making it possible to merge with the conduction and the valence bands respectively to produce partially filled bands resulting conductivity like metals. The template based technique for synthesis of microwires epitomize a basis to the layer-by-layer coplanar deposition of PPy during oxidative polymerization comprising more regular and higher crystalline structure than those produced electrochemically.
Accomplishing the synthesis of PPy in the restricted dimensions of cylindrical pores of template, the polymer chains are forced to align within the host mould, hence increase in conductivity can be expected due to increase in conjugation length and orientation of polymer chains.

4. Conclusions

Microwires of PPy has been successfully synthesized via chemical polymerization using the polycarbonate track etch membrane as template. By way of template method, cylindrical ordered microwires of uniform diameter and length have been prepared at room temperature. The electrical conductivity equal to 20.152 S/m has been obtained for these microwires. Various shapes and sizes of nano/micro PPy structures can be synthesized using this technique of template assisted chemical polymerization by altering the morphology of pores in TEM templates. In futuristic research, by combining the different doping elements in-situ during chemical polymerization, the conductivity of the PPy can be varied and low dimensional structures of new functional composite materials can be accomplished. The polycarbonate TEM impregnated with PPy microwires is observed as flexible, smooth and rugged surface which leads to it as potential substrate for holding biomolecules in biosensing and biomedical applications, as these materials are biocompatible.

Acknowledgements

The authors are thankful to Central Instrumentation Laboratory, Punjab University Chandigarh for providing SEM facility and to Department of Physics, National Institute of Technology, Kurukshetra for I-V characterization facility. The first author is also grateful to Guru Jambheshwar University of Science & Technology, Hisar for providing financial assistance in the form of Minor Research Project.

References

http://dx.doi.org/10.1155/2006/860413


http://dx.doi.org/10.1016/S0168-583X(01)00722-4

http://dx.doi.org/10.1016/0379-6779(96)80158-5


http://dx.doi.org/10.1007/s12648-009-0030-2

Chakarvarti, S.K., Vetter, J., 1998. Template synthesis - a membrane based technology for generation of
nano/micromaterials: a review. Radiation Measurements 29(2), 149-159.
http://dx.doi.org/10.1016/S1350-4487(98)00009-2

http://dx.doi.org/10.1007/s00542-009-0885-3


http://dx.doi.org/10.1016/S0168-583X(00)00455-9

http://dx.doi.org/10.1142/S0217984912502090

http://dx.doi.org/10.1016/j.aca.2005.10.011

http://dx.doi.org/10.3390/s110505087

http://dx.doi.org/10.1016/j.snb.2004.08.011

http://dx.doi.org/10.1023/B:JMSC.0000041719.33315.ab

Kumar, S., Chakarvarti, S.K., 2006. Electrodeposition of copper nanowires in ion-crafted membranes as templates. Digest Journal of Nanomaterials and Biostructures 1(4), 139-143.

http://dx.doi.org/10.1016/j.radmeas.2009.10.022


http://dx.doi.org/10.1016/S0379-6779(98)00060-5

http://dx.doi.org/10.1016/j.mser.2004.07.003

http://dx.doi.org/10.1016/0302-4598(95)01802-4

membrane fuel cells: dual-site mechanism of oxygen reduction reaction in alkaline media on cobalt−polypyrrole electrocatalysts. The Journal of Physical Chemistry C 114(11), 5049. doi:10.1021/jp910572g.


