

## Chemical synthesis of polypyrrole nano/microstructures using track etch membranes

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Among the different strategies to synthesize nanoscopic materials reported in the literature, *template synthesis* is an elegant approach [1–3]. This technique consists of including metallic or organic constituents inside the void spaces of nanoporous host materials. Though there now exists a huge range of hosts, track-etched membranes present a significant advantage because they lead to the production of different kinds of nanotubules and nanowires with monodisperse diameters and lengths. Martin and Hulteen [4–6] have used these membranes as templates to prepare nanofibrils composed of metals, semiconductors, and conducting polymers, most of their work has focused on the chemical synthesis of polypyrrole, polyaniline, and polymethylthiophene.

In the present work, the chemical growth of polypyrrole nanofibrils obtained from polycarbonate nanoporous particle track-etched membranes is studied. The morphologies of the obtained microstructures have been carefully analyzed using a scanning electron microscope. A two-probe method has been used to measure the electrical conductivity of template-synthesized polypyrrole microstructures.

The nuclear track filter used here as a template was of Makrofol KG foil (polycarbonate from Bayer AG), 60  $\mu\text{m}$  thick, having average pore diameter  $\sim 6 \mu\text{m}$  with pore density  $1 \times 10^6 \text{ m}^{-2}$ . This was prepared by irradiating the foil with  $^{238}\text{U}$ , energy ca. 13.64 MeV/n at 90 °C at the UNILAC facility available at GSI, Darmstadt, Germany, followed by chemical amplification of the damage trails by etching in 6N NaOH, at  $60 \pm 2^\circ \text{C}$  for 35 min. In order to produce see-through pores, optimum etch time and etch conditions were preset.

As shown in Fig. 1, the polycarbonate membrane was used as a dividing wall in a two-compartment cell. In the first compartment, an aqueous pyrrole solution (0.5 M) was added and allowed to diffuse through the membrane for 10 min prior to the introduction of the oxidant reagent ferric chloride (0.4 M) in the second compartment. The monomer and the oxidant reagent diffuse toward each other through the pores of the membrane

and react to yield the polymer. The polymerization process was continued for 1 hr 30 min.

For the morphological characterization of the polypyrrole microstructures by means of scanning electron microscopy (SEM), specimens were observed by dissolving the polycarbonate matrix in dichloromethane. The cleaned and dried samples were mounted on the specially designed aluminum stubs with the help of double sided adhesive tape and viewed under a “Jeol, JSM 6100 Scanning Microscope” at an accelerating voltage of 20 KV. Images were recorded on the photographic film in the form of negatives at different magnifications. Fig. 2 shows scanning electron micrographs of polypyrrole microstructures. Fig. 3 shows a scanning electron micrograph of a single polypyrrole microtube.

The electrical conductivity of the polypyrrole microstructures established inside the pores was obtained by measuring the bulk resistance across the filled membrane by a two-probe method. Since the polypyrrole surface layers on the membrane can contribute to the resistance measurement but cannot be completely removed because they ensure the contact between the polypyrrole nanostructures and electrical wires [7], we tried to limit the thickness of these surface layers. Cai *et al.* [7] indicated that such thin layers did not contribute to the membrane resistance.

One side of the membrane was held on the copper electrode and two copper wires contacted the other side of the membrane. Silver paste ensured a good contact and allowed specification of a well-defined cross-section for calculating the conductivity. The conductivity along a single fiber can be calculated from the resistance measurement that provides the bulk resistance of the composite membrane. Assistance  $R$  can be written as

$$1/R = 1/R_f + 1/R_m \quad (1)$$

where  $R_f$  is the parallel sum of the resistances of the conductive polymer fibrils and  $R_m$  is the resistance of

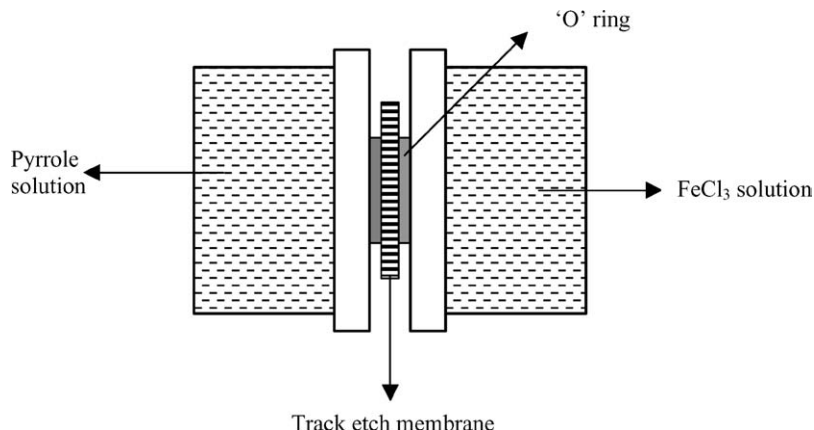


Figure 1 Two-compartment cell used to perform chemical polymerization of polypyrrole.

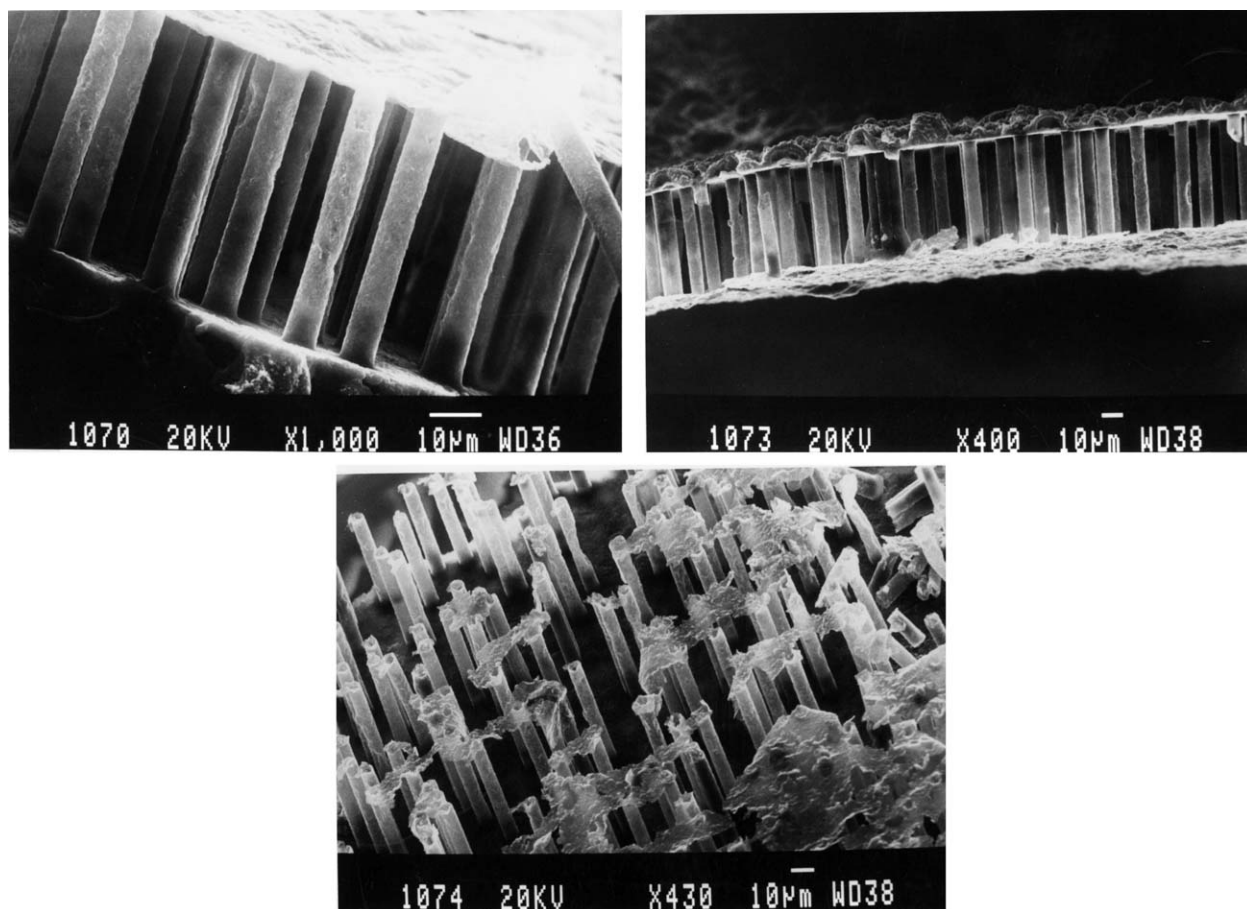


Figure 2 Scanning electron micrographs of polypyrrole microstructures.

the polycarbonate membrane.  $R_m$  can be neglected because  $R_m \gg R_f$ . So we can write the last equation,

$$1/R = 1/R_f = n/R_i \quad (2)$$

where  $n$  is the number of fibrils in the measurement area and  $R_i$  is the resistance of an individual fibril. Knowing the diameter ( $\phi$ ) and the length ( $L$ ) of the pores and from the calculated value of  $R_i$ , the fibril conductivity ( $\sigma$ ) can be determined by

$$\sigma = L/(R_i \pi \phi^2/4) \quad (3)$$

If the microstructures show a tubular morphology, the thickness of polypyrrole tubules must be taken into ac-

count in the calculation of conductivity by considering the outside diameter ( $\phi_o$ ) and the inside diameter ( $\phi_i$ ) of the tubule. In this case, the relationship (3) becomes

$$\sigma = L/[R_i \pi (\phi_o^2 - \phi_i^2)/4] \quad (4)$$

In the present work electrical conductivity of polypyrrole microtubules was calculated using Equation 4 and was found to be  $87 \text{ S cm}^{-1}$ .

The electrical properties of conducting polymers are determined by their electronic structure. Conduction results from the presence of polarons and bipolarons along the polymer chain. The charge transport occurs via mobility of these charges along segments of the

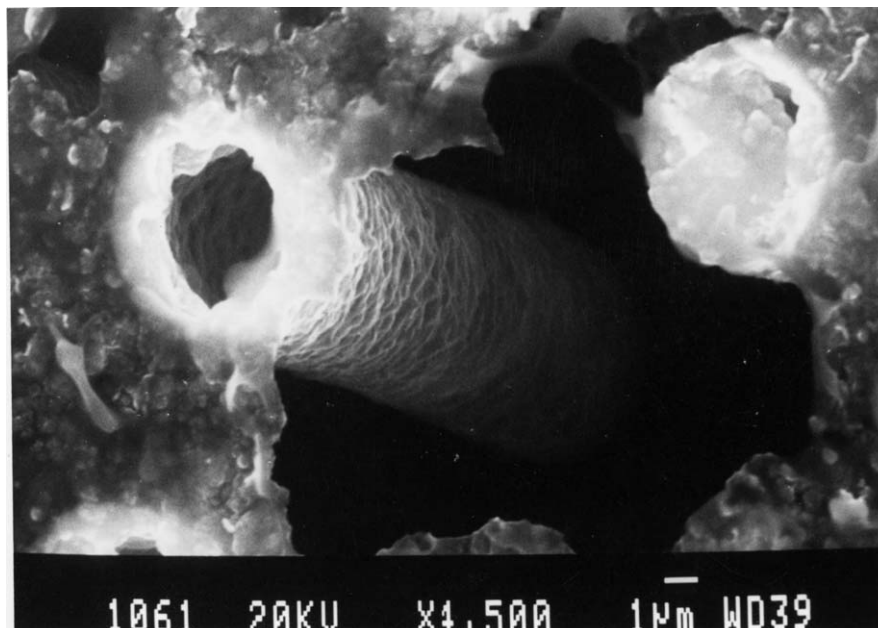


Figure 3 Scanning electron micrograph of single polypyrrole microtube.

conjugated polymer chains and by hopping of these charges from chain to chain. The electrical conductivity is dependent both on carrier concentration and the carrier mobility. The conductivity of the conjugated polymers is limited by the carrier mobility rather than by the carrier concentration. The carrier mobility depends on two factors: the interchain distance and the frequency of the interchain hopping. The frequency of the interchain hopping can be reduced either by increasing the conjugation length or by orienting the polymer chains. In a conjugated polymer, delocalization may be interrupted by the chain-ends, by the  $\alpha$ - $\beta$  carbon linkage, and/or by the other structural or conformational defects, which decrease the conjugation length and consequently the electronic conductivity of the polymer. Thus, by realizing the synthesis of conducting polymers in the confined medium, here the nanopores of a template membrane, the polymer chains are forced to align within the environment of the host matrix and an enhancement of the conductivity can be expected. The polypyrrole initially deposited on the pore walls is highly oriented and has extended conjugation. The orientation derives from the templating effect of the underlying polycarbonate chains, which are highly ordered due to stretch orientation. Apparently, the surface acts as a template forcing the pyrrole monomers to be coplanar during bond formation. The planar configuration favors  $\alpha$ - $\alpha$  linkage, which results in an increase of the conjugation length.

In conclusion, chemical synthesis of polypyrrole has been performed using the polycarbonate track etch membranes as templates. By using this method, perfectly cylindrical polypyrrole tubules of diameter  $6 \mu\text{m}$  have been successfully prepared. At room temperature, a conductivity value of  $87 \text{ S cm}^{-1}$  has been obtained for these tubules.

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